

Accurate Spin-density based on the Domain-based Local Pair-Natural Orbital Coupled-Cluster Theory

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Exploiting locality in the electron correlation reduces the computational cost for solving the Coupled-Cluster (CC) equations which give the superior results to the widely-used Density Functional Theories (DFTs). Recently, we have proposed a series of CC formulations in the domain-based local pair-natural orbital framework (DLPNO-CCSD and DLPNO-CCSD(T)) which are designed to reproduce approximately 99.9 % of the canonical correlation energy. In our previous work, the DLPNO-CCSD method has been extended to the high-spin open-shell reference and shown to possess comparable accuracy to the closed-shell counterpart [M. Saitow *et al.*, J. Chem. Phys. 146, 164105 (2017)]. Importantly, when applied to the closed-shell species, the open-shell DLPNO-CCSD gives nearly identical results to the closed-shell dedicated implementation. The so-called Λ -equations have been formulated in the DLPNO framework for the closed-shell species as an exact derivative of the DLPNO-CCSD Lagrangian with respect to the PNO-based cluster amplitudes [D. Datta *et al.*, J. Chem. Phys. 145, 114101 (2016)]. In this paper, we extend the DLPNO-based Lagrangian scheme to the high-spin open-shell reference cases, thus enabling the accurate computation of the electron- and spin-densities for large open-shell species. We apply this newly developed approach to various first-order electronic and magnetic properties such as isotropic and anisotropic components in the hyperfine coupling interactions and the electric field gradient. We demonstrate that the DLPNO-CCSD results converge towards the respective canonical CC density and also that the DLPNO-CCSD-based properties are more accurate than the conventional DFT results in real-life applications. The additional computational cost is less than one energy evaluation in the DLPNO-CCSD framework.

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I. INTRODUCTION

The accurate computation of the magnetic and electronic properties plays a central role for interpretation of the various molecular spectra such as electron paramagnetic resonance (EPR), electron spin resonance (ESR), and Mössbauer spectroscopies,¹⁻³ which provide accurate and detailed information on the molecular electronic structure. The Coupled-Cluster with Singles and Doubles (CCSD) model^{4,5} and its simplified variant (Quadratic Configuration Interaction with Singles and Doubles; QCISD)⁶ are known to give hyperfine coupling (HFC) tensors which are in near quantitative agreement with the experimental values.⁷⁻¹³ Property calculations based on the CCSD/QCISD wave functions have been made feasible by the so-called Lagrangian technique.¹⁴⁻¹⁸ In this approach, one makes the CC correlation energy functional stationary in order to satisfy the generalized Hellmann-Feynman condition.¹⁹ As a result, in addition to having to solve the cluster equations, one has to solve another set of many-body equations, the so-called Λ -equations; The CCSD Λ -equations define the left side amplitudes that coincide with the right side CCSD cluster amplitudes. Moreover, by solving the Λ -equations for higher-lying roots, one can obtain the electronic excitation energies and the corresponding wave functions in the CC linear-response (CC-LR) framework.²⁰⁻²² Additionally to the single reference approaches, there have been numerous efforts to establish the multi-reference response theories for calculating accurate EPR/ESR parameters for low-spin open-shell systems.²³⁻²⁹

As is well known, the computational costs for solving the CCSD (or QCISD) equations increases as $O(N^6)$, where N is a measure of system size. Therefore, despite its excellent accuracy, the applicability of CCSD has been limited to systems composed of not more than approximately 10 – 30 atoms. Given the fact that Hartree-Fock (HF) theory is grossly inaccurate for HFCs and electric field gradients (EFGs), density-functional linear response theory has been the only practical choice for calculating these spectroscopic parameters.

In order to overcome the steep computational scaling, we have recently developed a series of reduced-scaling CCSD method in the local pair-natural orbital framework (LPNO-CCSD).³⁰⁻³² Later, a more sophisticated scheme was proposed that leads to linear-scaling with respect to computational resources (DLPNO-CCSD and perturbative triple excitations; DLPNO-CCSD(T)).^{33,34} Even more recently, we have redesigned the whole DLPNO scheme^{35,36} and the DLPNO-CCSD(T) methods have been extended to the high-spin open-shell reference function in a consistent manner to the closed-shell implementation;³⁷ This ensures that, when applied to the closed-shell systems,

the open-shell DLPNO-CCSD gives chemically identical results to its closed-shell variant. The computational cost of the newer version of the DLPNO-CCSD(T) method scales linearly with respect to the system size for the closed-shell species while recovering approximately 99.9 % of the canonical CCSD(T) correlation energy. For open-shell species, on the other hand, the scaling of the DLPNO-CCSD(T) becomes linear to quadratic. Still, for large open-shell systems, the actual CPU time spent for the DLPNO-CCSD(T) is quite comparable to or even shorter than that for the preceding self-consistent field (SCF) procedure.

The developments of the local-correlation theories have been a very active research field and there have been many important efforts including Pulay *et al.*,^{38–40} Werner and co-workers,^{41–50} Hättig *et al.*^{51–58} and many others.^{59–70} Korona, Schütz and co-workers developed a series of response theory based on the local version of the second-order CC (CC2) wave functions.^{71–74} Crawford *et al.* demonstrated the accuracy of various local approximations in CCSD-LR framework using a simulated PNO code.^{75–78} Importantly, they have figured out that especially for those molecules which possess three-dimensional, cage-like structure, the pair and PNO truncation thresholds should be tightened by several orders of magnitude to obtain a good agreement with the canonical results at the PNO-based CC2 level.⁷⁸ Another important finding of theirs is that also for the property calculations use of PNOs for truncating the virtual space certainly outperforms the orbital specific virtual (OSV) formalism by Chan *et al.*^{47,48,61,62} to achieve a certain accuracy with use of a minimal set of virtual orbitals.

For the closed-shell reference, as an exact derivative of the DLPNO-CCSD Lagrangian with respect to the PNO-based cluster amplitudes, the DLPNO-CCSD Λ -equations have been formulated⁷⁹ and implemented in ORCA 4.0 program suite.⁸⁰ When applied to dipole moment calculations, the DLPNO-CCSD Lagrangian scheme was shown to reproduce typically 98 – 99 % of the canonical CCSD results. However, achieving this accuracy required tighter truncation thresholds than are used in the correlation energy calculations. In this paper, we extend the DLPNO-based Lagrangian scheme to the high-spin open-shell reference functions thus enabling the accurate computations of spin-density and the first-order magnetic properties for large open-shell species. We first demonstrate the DLPNO-CCSD densities converge towards their canonical counterparts. Secondly, we show that the computational effort remains reasonable and does at most double the time for a single point DLPNO-CCSD calculation. Finally, it is shown that the DLPNO-CCSD results are superior in accuracy to those delivered by a variety of modern density functionals.

II. THEORY

A. The Λ -Equations for Unrelaxed CCSD Densities

The CCSD wave function is defined with an exponential operator acting on the reference HF function (Ψ_0)

$$|\Psi_{\text{CCSD}}\rangle = e^{T_1+T_2} |\Psi_0\rangle \quad (1)$$

where one- and two-body excitation operators are defined as

$$T_1 = \sum_{ia} t_a^i \{a^a a_i\} \quad (2)$$

and

$$T_2 = \frac{1}{4} \sum_{ijab} t_{ab}^{ij} \{a^a a^b a_j a_i\}, \quad (3)$$

respectively. Throughout this paper, we use $ijkl \dots$ and $abcd \dots$ to represent occupied and virtual spin-orbitals, respectively. Symbols $wxyz$ are used for the generic single electron functions. The fermionic creation (annihilation) operator on orbital i is represented by a^i (a_i). In Eqs. (2) – (3), $\{\dots\}$ stands for a string of normal-ordered fermionic operators with respect to reference state. With Eq. (1), the CCSD energy and the residual equations read

$$E_{\text{CCSD}} = \langle \Psi_0 | \bar{H} | \Psi_0 \rangle, \quad (4)$$

$$r_a^i = \langle \Psi_i^a | \bar{H} | \Psi_0 \rangle, \quad (5)$$

and

$$r_{ab}^{ij} = \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle \quad (6)$$

where similarity-transformed Hamiltonian is given as $\bar{H} = e^{-T_1-T_2} H e^{+T_1+T_2}$. By satisfying the following conditions,

$$\mathbf{R}_1(\mathbf{T}_1, \mathbf{T}_2) \rightarrow 0 \quad (7)$$

$$\mathbf{R}_2(\mathbf{T}_1, \mathbf{T}_2) \rightarrow 0 \quad (8)$$

one can obtain a set of t_1 and t_2 CCSD amplitudes. Therefore, once the CCSD residual equations (Eqs. (7) – (8)) are solved, one can see that the following quantity serves as a CCSD energy functional

$$\tilde{F}[\mathbf{T}_1, \mathbf{T}_2, \mathbf{\Lambda}_1, \mathbf{\Lambda}_2, H] = E_{\text{CCSD}} + \sum_{ia} \lambda_i^a r_a^i + \frac{1}{2!} \sum_{ijab} \lambda_{ij}^{ab} r_{ab}^{ij}. \quad (9)$$

Having defined one- and two-body de-excitation operators,

$$\Lambda_1 = \sum_{ia} \lambda_i^a \{a^i a_i\} \quad (10)$$

and

$$\Lambda_2 = \frac{1}{4} \sum_{ijab} \lambda_{ij}^{ab} \{a^i a^j a_b a_a\}, \quad (11)$$

respectively, and using Eqs. (4) – (6), the CCSD energy functional (Eq. (9)) can be rewritten into a more concise form

$$\tilde{F}[\mathbf{T}_1, \mathbf{T}_2, \mathbf{\Lambda}_1, \mathbf{\Lambda}_2, H] = \langle \Psi_0 | (1 + \Lambda_1 + \Lambda_2) \tilde{H} | \Psi_0 \rangle. \quad (12)$$

If Eq. (9) is made stationary with respect to all the parameters,

$$\frac{\partial \tilde{F}}{\partial \Lambda_n} \rightarrow 0 \quad (\forall n = \{1, 2\}) \quad (13)$$

$$\frac{\partial \tilde{F}}{\partial \mathbf{T}_n} \rightarrow 0 \quad (\forall n = \{1, 2\}) \quad (14)$$

the first derivative of the CCSD energy with respect to an arbitrary external perturbation (X) can be written as

$$\begin{aligned} \frac{\partial \tilde{F}}{\partial X} &= \frac{\partial \tilde{F}}{\partial H} \frac{\partial H}{\partial X} + \sum_{n=1,2} \left(\frac{\partial \tilde{F}}{\partial \mathbf{T}_n} \frac{\partial \mathbf{T}_n}{\partial X} + \frac{\partial \tilde{F}}{\partial \Lambda_n} \frac{\partial \Lambda_n}{\partial X} \right) \\ &= \frac{\partial \tilde{F}}{\partial H} \frac{\partial H}{\partial X}. \end{aligned} \quad (15)$$

From definition of \tilde{F} (Eq. (12)), one further obtains the following expression

$$\begin{aligned} \frac{\partial \tilde{F}}{\partial X} &= \langle \Psi_0 | (1 + \Lambda_1 + \Lambda_2) e^{-T_1 - T_2} \frac{\partial H}{\partial X} e^{+T_1 + T_2} | \Psi_0 \rangle \\ &= \sum_{wx} D_{wx}^{\text{CCSD}} \frac{\partial f_{wx}}{\partial X} + \frac{1}{2} \sum_{wxyz} \frac{\partial (wy|xz)}{\partial X} D_{wx,yz}^{\text{CCSD}} \end{aligned} \quad (16)$$

where two-electron integrals in Mulliken notation are used. In Eq. (16), the perturbation-independent, unrelaxed CCSD densities can be determined by

$$D_{wx}^{\text{CCSD}} = \langle \Psi_0 | (1 + \Lambda_1 + \Lambda_2) e^{-T_1 - T_2} \{a^w a_x\} e^{+T_1 + T_2} | \Psi_0 \rangle \quad (17)$$

and

$$D_{wx,yz}^{\text{CCSD}} = \langle \Psi_0 | (1 + \Lambda_1 + \Lambda_2) e^{-T_1 - T_2} \{a^w a^x a_z a_y\} e^{+T_1 + T_2} | \Psi_0 \rangle. \quad (18)$$

The first stationary condition (Eq. (13)) is identical to the CCSD amplitude equations while the second (Eq. (14)) defines an additional set of equations, which are known as Λ -equations

$$\mathbf{L}_n := \frac{\partial \tilde{F}}{\partial \mathbf{T}_n} \quad (\forall n = \{1, 2\}). \quad (19)$$

It is well-known that the Λ -equation is closely-related to the left-side equations of the equation-of-motion (EOM) CCSD methods^{81,82} for the excitation energy calculations.²² One can derive the explicit forms of Eq. (19) either diagrammatically or by taking derivative of the CCSD energy functional (Eq. (9)) with respect to the CCSD t -amplitudes. Expectation value of any first order properties, such as isotropic and anisotropic components in HFC tensors, can be calculated at CCSD level by taking a trace

$$\langle X \rangle_{\text{CCSD}} = \text{trace} \langle \mathbf{X} \mathbf{D}_{\text{CCSD}} \rangle \quad (20)$$

where \mathbf{X} is a matrix representation of operator X in a given single electron basis.

B. Summary of the Open-Shell DLPNO-CCSD Formalism

In the DLPNO-CCSD formalism, we employ a dressed Hamiltonian in the formulation of the CCSD residual vector

$$\mathbf{R}(\mathbf{T}) := \tilde{\mathbf{H}}(\mathbf{T})\mathbf{T} + \mathbf{\Theta}(\mathbf{T}) \quad (21)$$

or equivalently

$$\mathbf{R}(\mathbf{T})_m := \sum_{n=\{0,1,2\}} \tilde{\mathbf{H}}_{mn}(\mathbf{T})\mathbf{T}_n + \mathbf{\Theta}_m(\mathbf{T}) \quad (\forall m = \{1, 2\}) \quad (22)$$

where $\tilde{\mathbf{H}}$ and $\mathbf{\Theta}$ represent the dressed Hamiltonian matrix with t -amplitudes and the several explicitly non-linear terms which cannot be used to form the dressed integrals, respectively. In this

particular factorization of the CCSD residual, most of the terms originate from the first term in Eq. (21) and they take the identical structure to those in σ -vector equation for CISD model. The explicit formulas of Eq. (21) for RHF- and UHF- cases are found in Refs. 30, 31, 33, and 34 and Refs. 32 and 37, respectively. In the open-shell DLPNO-CCSD method, we solve the UHF-CCSD equations in the DLPNO basis for the electron pairs which survived the multilevel pair-energy-based screening while the reference wave function is assumed to be a Slater determinant composed of a set of doubly-occupied MOs (DOMOs) and a few singly-occupied MOs (SOMOs). Hereafter, the CCSD residual vectors, t - and λ -amplitudes may be simply written as

$$\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2), \quad (23)$$

$$\mathbf{T} = (\mathbf{T}_1, \mathbf{T}_2) \quad (24)$$

and

$$\mathbf{\Lambda} = (\mathbf{\Lambda}_1, \mathbf{\Lambda}_2), \quad (25)$$

respectively, in the interest of clarity.

In the high-spin open-shell DLPNO formalism, the PNOs for DOMO-DOMO (ij), SOMO-DOMO (pi) and SOMO-SOMO (pq) pairs are generated by pair-functions based on the single-reference variant of N-electron valence perturbation theory (NEVPT) wave function.^{83,84} For instance, for ij pairs, the PNOs are constructed by

$$|a_{ij}\rangle = \sum_{\mu_{ij}} d_{a_{ij},\mu_{ij}} |\mu_{ij}\rangle \quad (26)$$

where μ_{ij} represents a set of non-redundant PAOs constructed in ij pair-domain which is a union of each of orbital domains for i and j . For diagonal electron pairs, we define the so-called singles PNOs which are used to expand t_1 -amplitudes and the related quantities

$$|a_i\rangle = \sum_{\mu_i} d_{a_i,\mu_i} |\mu_i\rangle. \quad (27)$$

In the second-generation of DLPNO implementations, the orbital domains are determined by analyzing the differential overlap integrals (DOIs) between occupied orbitals and the (redundant) PAOs

$$(\text{DOI})_{i\mu} = \sqrt{\int |\phi_i(\mathbf{r})|^2 |\phi_{\mu}(\mathbf{r})|^2 d^3\mathbf{r}}. \quad (28)$$

For a given occupied orbital i , all the atoms at least one of whose PAOs has a larger DOI with i than the threshold (TCutD0) are included in the orbitals domain for i . Typically, this results in larger orbital domains than those in the conventional approach based on Mulliken charges, thus leading to a more stable description of the electronic structure. The advantage of this particular formalism of the open-shell PNOs over a more straightforward Ansatz based on the unrestricted Møller-Plesset perturbation (UMP) theory are that (1) convergence to the closed-shell MP1-PNOs is naturally ensured and (2) the same-spin and the different-spin pairs are treated in a more well-balanced manner. In Eq. (26), the PAO-PNO coefficients are determined by diagonalizing the pair-density for the virtual space

$$(D_{ij})_{\mu_{ij}, \nu_{ij}} = \langle \Psi_{ij} | E_{\mu_{ij}}^{\nu_{ij}} | \Psi_{ij} \rangle \quad (29)$$

for ij pairs where Ψ_{ij} and E represent the NEVPT1 pair-function and the spin-free excitation operators, respectively. The eigenvalues of Eq. (29) correspond to the occupation number of the PNOs. Only those PNOs which possess larger occupancy than threshold (TCutPNO) are kept and proceed to the succeeding PNO integral generations. The singles PNOs are also determined by diagonalizing the diagonal pair-density defined with Ψ_{ii} . A tighter truncation threshold is used to truncate the singles PNOs ($0.03 \times \text{TCutPNO}$).

In the open-shell DLPNO-CCSD procedure, the pair-energies for ij pairs are first evaluated at the dipole-approximated strongly-contracted NEVPT2 level and those pairs which possess negligibly small pair-energies are screened out. The surviving electron pairs are again examined through pair-energy-based screening at two-step semi-canonical NEVPT2 level. The PNOs are constructed for all the pairs which have survived all of the pair-energy-based screening. An important technicality in the open-shell DLPNO method is that, after the PNOs are constructed, the SOMOs are also included in the PNO space of every electron pair. This is because SOMOs serve as virtual orbitals for β electrons while they are occupied by α electrons. Having SOMOs in both occupied and PAO/PNO space drastically simplifies the PNO integral generation and transformation steps even though this choice introduces a small amount of redundancy.

The following 0 – 4 external PNO integrals are generated for those pairs which enter to the DLPNO-CCSD step: $(\bar{a}_{ij}\bar{c}_{ij}|\bar{b}_{ij}\bar{d}_{ij})$, $(k\bar{a}_{ij}|\bar{b}_{ij}\bar{c}_{ij})$, $(j\bar{a}_{ij}|\bar{b}_{ij}\bar{c}_{ij})$, $(i\bar{a}_{ij}|\bar{b}_{ij}\bar{c}_{ij})$, $(i\bar{a}_{ij}|j\bar{b}_{ij})$, $(i|j\bar{a}_{ij}\bar{b}_{ij})$, $(ik|j\bar{a}_{ij})$, $(jk|i\bar{a}_{ij})$, $(i|j|k\bar{a}_{ij})$, $(ik|jl)$ where the indices with overbar represent the spin-orbitals for β electrons; \bar{a}_{ij} stands for an union of the PNOs for ij pair and SOMOs. The number of such pairs scales linearly with respect to the number of atoms, and thus, all the computational steps

after the PNO generations shows linear-scaling behaviour in computational time, memory and disk requirements. In each step in the DLPNO-CCSD iterations, the CCSD residual vectors, Eq. (21), for the surviving pairs are constructed in the PNO basis. Importantly, when applied to the closed-shell species, the open-shell DLPNO-CCSD produces chemically identical results to the closed-shell dedicated formulation. The truncation parameters in DLPNO procedure are listed in Table I. By setting all the parameters in Table I zero, the open-shell DLPNO methods converge to the canonical counterpart.

Translation of canonical CCSD equations into the DLPNO basis is rather straightforward. For instance, a term in UHF-DLPNO-CCSD residual equations,

$$r_{ab}^{ij} \leftarrow \sum_{cd} \left[(ac|bd) - \sum_k (kd|ac) t_b^k + \sum_k (kc|bd) t_a^k \right] \tau_{ab}^{ij} \quad (30)$$

where τ refers to a dressed amplitude $\tau_{ab}^{ij} = t_{ab}^{ij} + t_a^i t_b^j - t_a^j t_b^i$, reads, in DLPNO basis,

$$r_{a_{ij}b_{ij}}^{ij} \leftarrow \sum_{c_{ij}d_{ij}} \left[(a_{ij}c_{ij}|b_{ij}d_{ij}) - \sum_{\{k\} \cap \{ij\} \neq \{0\}} (kd_{ij}|a_{ij}c_{ij}) \sum_{b_k} S_{b_{ij}b_k} t_{b_k}^k + \sum_{\{k\} \cap \{ij\} \neq \{0\}} (kc_{ij}|b_{ij}d_{ij}) \sum_{a_k} S_{a_{ij}a_k} t_{a_k}^k \right] \tau_{c_{ij}d_{ij}}^{ij}. \quad (31)$$

The dressed amplitude in PNO basis is defined as

$$\tau_{a_{ij}b_{ij}}^{ij} = t_{a_{ij}b_{ij}}^{ij} + \sum_{a_i, b_j} S_{a_{ij}a_i} t_{a_i}^i t_{b_j}^j S_{b_{ij}b_j} - \sum_{a_j, b_i} S_{a_{ij}a_j} t_{a_j}^j t_{b_i}^i S_{b_{ij}b_i}. \quad (32)$$

In Eq. (31), the loop over k runs only those singles pair which has overlapping domain with the driving pair ij . All of the PNO integrals in Eq. (31) are subsets of those for β electrons. Hence, if necessary, the PNO integrals are carved out into an appropriate shape so that the tensor contractions are carried out by optimized BLAS functions. Since the PNOs belonging to different pairs are not orthogonal, PNO overlap matrices should be introduced. A non-triviality of translation into the DLPNO basis is that the contraction of the t_2 -amplitude and the dressed 2-external PNO integrals. In canonical basis, one of such terms takes form as

$$r_{ab}^{ij} \leftarrow \sum_{kc} t_{ac}^{ik} [(jb|\tilde{k}c) - (jk|cb)]. \quad (33)$$

In the DLPNO basis, linear and non-linear (dressing) parts in Eq. (33) are treated separately;

$$r_{a_{ij}b_{ij}}^{ij} \leftarrow \sum_k \sum_{c_{ik}} [(kc_{ik}|jb_{ij}) - (jk|c_{ik}b_{ij})] t_{a_{ik}c_{ik}}^{ik} S_{a_{ij}a_{ik}} + \sum_{\{k\} \cap \{ij\} \neq \{0\}} S_{a_{ij}a_{ik}} t_{a_{ik}c_{ik}}^{ik} S_{c_{ik}c_{jk}} \left(\Delta \tilde{K}(\mathbf{T}) \right)_{b_{jk}c_{jk}}^{jk} S_{b_{jk}b_{ij}} \quad (34)$$

where the dressed 2-external PNO integral is divided into an undressed part and a dressing

$$(kc|\tilde{j}b) \leftarrow (kc|jb) + \left(\Delta\tilde{K}(\mathbf{T})\right)_{bc}^{jk}. \quad (35)$$

This particular choice drastically reduces the PNO and pair truncation errors, enabling to recover more than 99.9 % of the canonical CCSD correlation energy. The semi-joint PNO integrals appearing in the first term in Eq. (34) are generated directly from the PAO integrals for all the possible combinations of ij , ik and jk pairs. On the other hand, the dressing part (the second term in Eq. (34)) are calculated by simple projection via PNO overlap matrices and the range of k is restricted to singles pairs whose domain is overlapping with ij pair as in case of other terms.

C. The DLPNO-CCSD Λ -Equations for Open-Shell Species

There are two strategies to arrive at the DLPNO-CCSD Λ -equations. The most straightforward way is to translate the canonical CCSD Λ -equations into the DLPNO basis. However, there is no unique way of translating the canonical CCSD equations into PNO basis. Therefore, a more consistent way of obtaining the DLPNO-CCSD Λ -equations may be to directly differentiate the DLPNO-CCSD energy functional with respect to PNO t -amplitudes as addressed in Ref. 79. By substituting the DLPNO-CCSD residual vector in the dressed Hamiltonian formalism (Eq. (21)) into the definition of \tilde{F} (Eq. (12)), one can write the DLPNO-CCSD energy functional

$$\tilde{F}[\mathbf{T}, \mathbf{\Lambda}, H] = E_{\text{CCSD}} + \sum_{m,n=\{0,1,2\}} \mathbf{\Lambda}_m^\dagger \tilde{\mathbf{H}}_{mn}(\mathbf{T}) \mathbf{T}_n + \sum_{m=\{1,2\}} \mathbf{\Lambda}_m^\dagger \mathbf{\Theta}_m(\mathbf{T}). \quad (36)$$

By taking derivative of Eq. (36), one can obtain the DLPNO-CCSD Λ -equations

$$\begin{aligned} \mathbf{L}_l &= \frac{\partial \tilde{F}}{\partial \mathbf{T}_l} \\ &= \frac{\partial E_{\text{CCSD}}}{\partial \mathbf{T}_l} + \sum_{m=\{1,2\}} \mathbf{\Lambda}_m^\dagger \tilde{\mathbf{H}}_{ml}(\mathbf{T}) + \sum_{m,n=\{1,2\}} \mathbf{\Lambda}_m^\dagger \frac{\partial \tilde{\mathbf{H}}_{mn}(\mathbf{T})}{\partial \mathbf{T}_l} \mathbf{T}_n + \sum_{m=\{1,2\}} \mathbf{\Lambda}_m^\dagger \frac{\partial \mathbf{\Theta}_m(\mathbf{T})}{\partial \mathbf{T}_l}. \end{aligned} \quad (\forall l = \{1, 2\}) \quad (37)$$

Note that terms arising from the first two terms in Eq. (37) essentially take the same structure as those terms from the first term in Eq. (22). The first term introduces the Hamiltonian matrix elements coupled to the reference manifolds ($\langle \Psi_i^a | H | \Psi_0 \rangle$ and $\langle \Psi_{ij}^{ab} | H | \Psi_0 \rangle$). The only difference from the t -equations consists in that, in the second term of Eq. (37), the dressed Hamiltonian with t -amplitudes, which is not symmetric, appears to be transposed in comparison with the t -amplitude

equations (Eq. (22)). The third and fourth terms in Eq. (37) are rather non-trivial and caused by the non-linearity of the CCSD Ansatz. By defining additional dressing of the integrals with t -amplitudes, one can simply obtain the actual working equations of the PNO-based Λ -equations. Since the DLPNO-based Λ -equations are derived from the DLPNO-CCSD residual equations, no additional set of PNO integrals are needed. Actually, the first two terms in Eq. (37) can be implemented by reusing the existing codes for solving the DLPNO-CCSD t -amplitude equations with a few minor modifications. Moreover, the doubles terms in the third and fourth terms in Eq. (37) often take similar structure to those terms in Eq. (22). Since Λ -equations are a set of linear-equations with respect to the λ -amplitudes, all the dressings appear in Eq. (37) only uses t -amplitudes.

The working equations for the UHF-DLPNO-CCSD Λ -equations have been derived using the same strategy as in the development of the RHF variant.⁷⁹ By taking advantage of the dressed Hamiltonian formalism of the DLPNO-CCSD, the Λ -equations are programmed such that a maximum amount of the codes for solving the UHF-DLPNO-CCSD t -amplitudes equations is reused. This strategy had enabled a rapid development of the DLPNO-CCSD response program.

III. RESULTS AND DISCUSSION

A. Computational Details

All the calculations were performed using the development version of ORCA 4.1 in which the open-shell DLPNO-CCSD Λ -equations are implemented. In all of the calculations, the AutoAux procedure⁸⁵ was used for the local resolution-of-the-identity (RI) treatment^{86–89} of the two-electron integrals in the DLPNO procedure.

IV. DISCUSSION

A. Accuracy of the DLPNO-based unrelaxed properties in comparison with the canonical CCSD

In the development of the DLPNO-CCSD response theory for closed-shell species,⁷⁹ we have already learned that, in general, the accuracy of the computed properties is more sensitive than the total energy. The most important truncation threshold is the TCutPNO parameter, which controls

the truncation of the PNO space for each occupied orbital pair. The default values for the remaining parameters such as TCutMKN, TCutDO and TCutPairs, which are shown in Table I, can be safely used to produce the desired accuracy. Therefore, in this section, we examine the proper set of PNO truncation threshold for the various open-shell properties, with special emphasis on the HFC and EFG tensors.

After an extensive amount of numerical experiments, we concluded that (1) the singles PNOs and (2) the PNOs for those pairs involving at least one core orbitals or SOMOs, such as core-core, core-valence, SOMO-DOMO, and SOMO-SOMO pairs, play an important role for accurate computation of spin-density at the position of nuclei that is proportional to the isotropic component of the HFCCs. Bistoni *et al.*⁹⁰ have proposed use of a tighter PNO truncation threshold for accurately taking into account the core-core and core-valence effects in the DLPNO framework thus introducing a scaling factor on TCutPNO for those pairs involving at least one core orbitals, which is called TScalePNOCore. In Ref. 90, they have optimized the scaling factor such that with the default TCutPNO threshold more than 99.9 % of the canonical CCSD correlation energy is recovered, obtaining TScalePNOCore equal to 1.0×10^{-2} as the default settings. Analogously, in this work, we introduce a new scaling factor for the TCutPNO threshold for pairs involving at least one SOMO which we call TScalePNOSOMO. A new set of truncation parameters we propose for accurate computation of various magnetic and electronic properties are shown in Table II in comparison with the conventional NormalPNO and TightPNO settings. In Default1 settings, the TCutPNO threshold is set to 1.0×10^{-7} as in case of TightPNO while in Default2 the TCutPNO is one order of magnitude tightened.

In Table III the DLPNO-based isotropic and anisotropic values of the HFCCs computed with Default1 and Default2 settings and the errors relative to the canonical CCSD results are shown for 58 atoms in 28 small radical species.⁹¹ The cc-pVQZ⁹² and cc-pwCVQZ⁹³ basis sets for hydrogen atoms and the heavier atoms were used, respectively. The geometries for those 28 radical species were taken from Ref. 91. As can be seen from Table III, with Default1 settings, the average absolute error (AAE) from the canonical CCSD values is 2.2 MHz for the isotropic HFCCs while those for the anisotropic components are approximately one order of magnitude smaller. For several atoms which possess large absolute value of the isotropic HFCCs, relatively large deviations up to 17.9 MHz, which is about 5.9 % of the untruncated value, can be found. By using tighter Default2 truncation settings, the AAEs for the isotropic HFCCs decrease up to 1.0 MHz while no drastic improvements are found in the anisotropic components. The largest deviation in

the computed isotropic HFCCs is reduced to 6.3 MHz (2.2 % of the canonical limit).

In Fig. ??, the AAEs of the DLPNO-based HFCCs are shown in comparison with those calculated by several major DFTs including B3LYP,⁹⁴ PBE,^{95,96} M06-2X,⁹⁷⁻⁹⁹ CAM-B3LYP¹⁰⁰ and B2PLYP.^{101,102} Although the B3LYP functional has been known to produce HFCCs and EFG tensors of decent accuracy,¹⁻³ the AAEs are one order of magnitude larger than those by the DLPNO-CCSD approach. The M06-2X functional gives the largest deviations up to 37.4 MHz in the isotropic HFCCs. The most accurate amongst the DFTs is B2PLYP which involves the second-order many-body correction even though the AAE for the isotropic HFCCs is about 11.8 MHz. Note that the B2PLYP results are based on the fully-relaxed densities obtained by solving the coupled-perturbed SCF equations.¹⁰²

In Fig. ??, the AAEs in EFG tensors, anisotropic and isotropic components of the HFCCs for all the atoms in phenoxyl-water complex as a function of TCutPNO threshold are shown while all the other thresholds are fixed to those of Default1 and Default2 settings. The geometry was also taken from Ref. 91. Even with TCutPNO= 1.0×10^{-7} , the AAEs are already well converged to the canonical limit for all of the three cases and it is less than 0.6 MHz for the isotropic HFCCs that is the most difficult case. As in case of Table III, the maximum deviation in the isotropic HFCCs with TCutPNO= 1.0×10^{-8} is decreased by about 40 %. Although use of the Default2 settings shows superb accuracy for all the cases, it is not a practical choice to employ such a tight TCutPNO for large systems.

We conclude that use of the Default1 settings, which employ similar set of truncation thresholds to the conventional TightPNO settings, produces HFCCs and EFGs of desirable accuracy while maximizing the balance between acceptable computational cost and high accuracy.

B. Hyperfine interactions in the solvated quinone radical

As in the previous contributions,^{91,103} we revisit the accuracy of the HFCCs on an explicitly-solvated model for the *p*-benzosemiquinone radical. The geometries of the radical with 4 and 20 water molecules were taken from Ref. 103. The anisotropic and isotropic HFCCs on the bridging hydrogens, carbonyl oxygens and quinone hydrogens computed by the DLPNO-CCSD with Default1 settings are shown in Table IV in comparison with DFT and experimental results. Since the quinone model with 20 water molecules is beyond the reach of the conventional B2PLYP implementation, the second-order perturbative part was computed with the RIJCOSX algorithm in

combination with the AutoAux procedure. The experimental values were taken from Refs. 104 and 105. In Fig. ??, the positions of the bridging hydrogen atoms are indicated in the model structure with 20 water molecules. The 4 water model is obtained by eliminating all the water molecules which are not containing bridging hydrogens.

In Table IV, it is seen that by increasing the number of water molecules the isotropic HFCC computed by the DLPNO-CCSD method on the bridging hydrogens is converging toward the experimental value. On the other hand, it is difficult to predict the sign of the experimental isotropic HFCC by the commonly-used DFTs. The anisotropic HFCCs on hydrogen atoms computed in Table IV are similar to each other and are in good agreement with the experimental values. The isotropic HFCCs by the DLPNO-CCSD and B2PLYP on oxygen atoms, which includes many-body perturbative correction, overshoot the experimental value while those by the other DFTs appear to be somewhat too low in magnitude. Nevertheless, the DLPNO-CCSD gives good agreement with the experimental values for all the cases especially when the more realistic 20 water model is employed. For the 20 water model, the DLPNO-CCSD iterations took 33 hours while the computational time for solving the DLPNO-CCSD Λ -equations was 40 hours on a single cluster node using 8 CPU cores of Xeon E5-2670[®] and 128 gigabyte of memory in total. Since the calculation was carried out in competitions with the other processes, there can be up to roughly 20 % of fluctuations in the computational times.

C. Accuracy of the DLPNO-based HFCCs for transition metal complexes

One of our ultimate goals in the development of the open-shell DLPNO-CC methodologies consists in providing a well-defined, *ab initio* ways of accurately calculating the metal HFCCs. This is motivated by the fact that for such systems the DFTs, which have been the most widely-used tools in computational chemistry, often give rather pronounced errors in the isotropic component of the HFCCs.¹⁰⁶ To test the performance of DLPNO-CCSD for metal HFCCs, we have chosen a set of transition metal complexes used in Ref. 106. We reoptimized the geometries using the TPSS functional¹⁰⁷ with the D3 correction.^{108,109} Solvation effects were treated only in the optimization process by the CPCM model.^{110,111} In the DFT calculations, the zeroth-order regular approximations (ZORA)^{112,113} were used for the relativistic correction and the ZORA-recontracted version of def2-TZVPP basis set^{114,115} was employed.

The DLPNO- and DFT-based results are given in Table V being compared with the experi-

mental values. In the DLPNO-CCSD calculations, the second-order Douglas-Kroll-Hess (DKH2) scalar-relativistic Hamiltonian^{116–118} was used in combination with DKH-recontracted basis. The property operator was relativistically-modified in the picture-change framework^{119–121} and the nuclei were treated as Gaussian distributions in the finite nucleus model.¹²² For those systems that possess metals in the d^8 and d^9 configurations such as Ni(II) and Cu(II) complexes, the second-order spin-orbit coupling (SOC) contributions are expected to be pronounced while the SOC components in the HFCCs have not been implemented in the DLPNO framework so far. This is because the second-order term requires an additional set of equations for the first-order perturbed cluster amplitudes.¹²³ To extract the first-order isotropic and anisotropic components from the experimental HFCCs, we exploited the ligand-field-based relationships¹²⁴ between the electronic g-value and the SOC contribution in the HFCC.^{106,125} Considering the fact that the g-values are observable, one can estimate the experimental value of the SOC contributions in the HFCCs by scaling the computed value;

$$A_{\text{SOC}}(n) = \frac{g_{\text{exp.}}(n)}{g_{\text{calc.}}(n)} \times A_{\text{SOC; calc.}}(n) \quad (38)$$

where n stands for the index for the principal values of the g-tensor. Note that the above relationship, Eq. (38), is based on an assumption that the HFC and g-tensors are colinear to each other and serves as a good approximation for our test sets. In Table V, for Ni(I) and Cu(II) complexes, we estimated the experimental values of the first-order HFCCs using the experimental and the computational g-values from Refs. 126–128 and by the B3LYP method,¹²⁵ respectively. The estimated values of SOC contributions for such complexes are given in the supplementary materials. All the other complexes have a metal in either of high-spin d^1 , d^3 and d^5 configurations and thus the experimental HFCCs are dominated by the first-order contributions. Since the SOC correction procedure is quite crude, there is a remaining uncertainty for the Ni(I) and Cu(II) complexes.

For those complexes with Cr(III), V(II), V(III) and Mn(II), the HFCC computed by the DLPNO-CCSD are all in good agreement with the experimental values and the largest deviation is less than 30 MHz for VO(acac)₂ (5.6 % of the canonical value) to which all the DFTs predict metal HFCCs with errors exceeding 100 MHz. In addition, for the metal HFCCs, the Default1 and Default2 settings gave quite similar results thus indicating that Default1 results are already well converged relative to the canonical CCSD. For the Ni(I) and Cu(II) complexes where sum of the isotropic and anisotropic components is roughly estimated by scaling the B3LYP-based g-values and A_{SOC} , the errors relative to the estimated values appear to be somewhat larger than

those for Cr, V and Mn complexes. We speculate that this is probably a result of the approximate extraction method. However, this can not be proven at the present stage. It is observed that the B3LYP and B2PLYP functionals appear to give metal HFCCs of decent accuracy as in case of the ligand HFCCs. However, a striking difference between the DLPNO-CC-based and the DFT-based metal HFCCs is that DLPNO-CCSD gives good agreement for all the cases while for some cases the DFTs give qualitatively wrong results such as B2PLYP and B3LYP results for VO(acac)₂.

We conclude that the unrelaxed DLPNO-CCSD density can be used to accurately calculate the metal HFCCs that are in semi-quantitatively good agreement with the experimental values especially for those systems where the second-order SOC contribution is small. For those metal complexes with the SOC contributions of non-negligible magnitude, the DLPNO-CCSD is estimated to give at least comparable accuracy to the B2PLYP and B3LYP functional which are known as the best DFTs for such purpose. Of course, once we have implemented the real DLPNO-based A_{SOC} term in future, we have to revisit those systems for a more thorough assessment of the accuracy of the method.

V. CONCLUSION

It has been known that the CCSD scheme provides not only accurate chemical energetics and the electronic wave function but also accurate magnetic and electronic properties. However, due to its high computational costs, the CCSD response theory has been applied only to small molecules composed of not more than a maximum of 30 atoms. In this work, we have derived a set of CC Λ -equations in a consistent way to the high-spin open-shell variant of the DLPNO-CCSD amplitude equations and implemented them into an efficient computer code as a part of the ORCA program suite. In the previous work by Datta *et al.*⁷⁹ on the development of the DLPNO-CC-based response theory for the closed-shell species, it was implied that for the accurate calculation of the dipole moment the PNO truncation threshold should be tightened by roughly one order of magnitude. In this work, we showed that, instead of tightening up the thresholds for the orbital pairs involving valence DOMOs, just tightening up the PNO thresholds for those pairs involving core orbitals or SOMOs leads to the HFC and EFG tensors of comparable accuracy to the canonical CCSD. The newly-developed scheme allows one to calculate the DLPNO-CCSD “unrelaxed” spin- and electron-densities as an exact derivative of the open-shell DLPNO-CCSD energy functional thus providing an accurate magnetic and electronic properties for large open-shell species.

We have applied the open-shell DLPNO response theory to various open-shell molecules including an explicitly-solvated model for *p*-benzosemiquinone radical and various third-row transition metal complexes. For the molecules composed only of light elements, using the Default1 truncation settings which is essentially a tailored TightPNO settings for the property computation, the AAEs from the canonical isotropic HFCCs are shown to be approximately 1.0 MHz. Using the DLPNO response theory, the isotropic HFCC on a bridging hydrogen atom in the explicitly solvated model for the quinone radical was computed accurately while not all of the DFTs succeeded to even produce the correct sign. The DLPNO-CCSD was shown to produce the isotropic metal HFCCs in a good agreement with the experimental values while it is certainly difficult to obtain the results of the same quality using the DFTs.

We believe that the newly-developed DLPNO response scheme for the open-shell species will be an attractive alternative to the widely-used DF-based response framework for computational chemists interested in the properties of open shell species. Ongoing work focuses on the various second-order properties including the g-tensors and the second-order SOC contribution to the HFC tensors.

SUPPLEMENTARY MATERIAL

See supplementary material for the estimated A_{SOC} using the experimental and B3LYP-based g-values for the Ni and Cu complexes.

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TABLE I. Major truncation parameters used in the DLPNO-CCSD methods and the values for default settings (NormalPNO).

Cutoff	Objective	Default Settings
TCutDO	Size of orbital and pair domains	1.00×10^{-2}
TCutMKN	Size of auxiliary domains	1.00×10^{-3}
TCutPair	Number of CCSD pairs	1.00×10^{-4}
TCutPNO	Number of PNOs	3.33×10^{-7}

TABLE II. The tightened truncation settings (Default1 and Default2) for the accurate computation of the electronic and magnetic properties in comparison with the conventional NormalPNO and TightPNO settings.

	TCutMKN	TCutDO	TCutPNO	TCutPNOSingles	TScalePNOCore	TScalePNOSOMO
NormalPNO	1.0×10^{-3}	1.0×10^{-2}	3.33×10^{-7}	9.99×10^{-9}	1.0×10^{-2}	1.0
TightPNO	1.0×10^{-4}	5.0×10^{-3}	1.00×10^{-7}	3.00×10^{-9}	1.0×10^{-2}	1.0
Default1	1.0×10^{-4}	5.0×10^{-3}	1.00×10^{-7}	0.00	1.0×10^{-3}	1.0×10^{-1}
Default2	1.0×10^{-4}	5.0×10^{-3}	1.00×10^{-8}	0.00	1.0×10^{-3}	1.0×10^{-1}

TABLE III: Isotropic and anisotropic HFCCs in MHz calculated by DLPNO-CCSD wave function using Default1 and Default2 settings without frozen core treatment. The absolute errors from the canonical CCSD values are shown in parenthesis.

Molecule	Atom	Default1								Default2							
		A _{iso}		A _{aniso} (1)		A _{aniso} (2)		A _{aniso} (3)		A _{iso}		A _{aniso} (1)		A _{aniso} (2)		A _{aniso} (3)	
BO	¹¹ B	1042.1	(4.3)	-26.9	(0.2)	-26.9	(0.2)	53.8	(0.4)	1039.5	(1.7)	-26.7	(0.0)	-26.7	(0.0)	53.4	(0.1)
	¹⁷ O	-10.8	(0.8)	21.3	(0.2)	21.3	(0.2)	-42.5	(0.4)	-10.1	(0.1)	21.4	(0.1)	21.4	(0.1)	-42.7	(0.2)
CN	¹³ C	643.8	(12.6)	-56.2	(0.0)	-56.2	(0.0)	112.5	(0.0)	633.6	(2.3)	-56.3	(0.1)	-56.3	(0.1)	112.6	(0.1)
	¹⁴ N	-22.6	(0.9)	39.8	(0.2)	-19.9	(0.1)	-19.9	(0.1)	-23.4	(0.1)	40.0	(0.0)	-20.0	(0.0)	-20.0	(0.0)
CO ⁺	¹³ C	1573.5	(11.2)	-49.4	(0.2)	-49.4	(0.2)	98.8	(0.5)	1565.1	(2.8)	-49.2	(0.1)	-49.2	(0.1)	98.4	(0.1)
	¹⁷ O	25.2	(0.7)	-74.3	(0.2)	37.1	(0.1)	37.1	(0.1)	25.6	(0.3)	-74.4	(0.1)	37.2	(0.1)	37.2	(0.1)
NO	¹⁴ N	20.6	(0.7)	-37.4	(0.2)	-39.8	(0.1)	77.2	(0.2)	20.9	(0.5)	-37.2	(0.0)	-39.7	(0.0)	77.0	(0.0)
	¹⁷ O	-34.3	(0.5)	61.9	(0.1)	72.4	(0.0)	-134.4	(0.1)	-34.3	(0.4)	62.0	(0.0)	72.4	(0.0)	-134.4	(0.1)
OH	¹⁷ O	-40.3	(3.3)	140.9	(0.1)	143.1	(0.1)	-284.0	(0.2)	-41.5	(2.1)	140.8	(0.0)	143.2	(0.2)	-284.0	(0.2)
	¹ H	-70.8	(0.7)	89.2	(0.1)	-15.7	(0.0)	-73.5	(0.1)	-70.8	(0.7)	89.2	(0.1)	-15.6	(0.0)	-73.5	(0.1)
HCO	¹ H	345.0	(0.2)	-16.5	(0.0)	-9.1	(0.0)	25.6	(0.0)	345.1	(0.2)	-16.5	(0.0)	-9.1	(0.0)	25.6	(0.0)
	¹⁷ O	-41.4	(0.8)	49.1	(0.1)	58.6	(0.2)	-107.7	(0.3)	-42.1	(0.1)	49.2	(0.0)	58.8	(0.0)	-107.9	(0.1)
	¹³ C	382.5	(0.2)	-49.9	(0.1)	-41.7	(0.2)	91.5	(0.3)	382.4	(0.0)	-49.8	(0.0)	-41.5	(0.0)	91.3	(0.1)
H2CO	¹³ C	-93.6	(1.2)	10.5	(0.1)	9.3	(0.1)	-19.7	(0.0)	-94.8	(0.0)	10.6	(0.0)	9.2	(0.1)	-19.8	(0.1)
	¹⁷ O	-58.3	(3.5)	117.4	(0.4)	143.4	(0.1)	-260.8	(0.5)	-60.8	(1.1)	117.3	(0.2)	143.3	(0.0)	-260.6	(0.3)
	¹ H	278.7	(0.8)	-10.2	(0.0)	-7.5	(0.0)	17.6	(0.0)	279.4	(0.1)	-10.2	(0.0)	-7.5	(0.0)	17.7	(0.0)
H2O ⁺	¹ H	-75.1	(0.4)	74.6	(0.1)	-21.8	(0.0)	-52.8	(0.1)	-75.0	(0.2)	74.6	(0.1)	-21.8	(0.1)	-52.8	(0.1)
	¹⁷ O	-72.0	(3.3)	149.1	(0.2)	154.1	(0.0)	-303.1	(0.2)	-73.4	(1.9)	149.1	(0.1)	154.1	(0.0)	-303.1	(0.2)
CH ₃	¹³ C	69.0	(3.7)	-78.4	(0.0)	-78.4	(0.0)	156.8	(0.0)	71.6	(1.2)	-78.4	(0.1)	-78.4	(0.1)	156.9	(0.1)
	¹ H	-69.6	(0.9)	38.4	(0.1)	2.9	(0.1)	-41.3	(0.0)	-69.5	(0.8)	38.5	(0.1)	2.9	(0.1)	-41.4	(0.0)
C ₃ H ₅	¹³ C	50.7	(1.7)	-50.2	(0.1)	-48.6	(0.1)	98.9	(0.1)	51.7	(0.7)	-50.3	(0.0)	-48.7	(0.0)	99.0	(0.0)
	¹³ C	-56.8	(0.1)	18.1	(0.1)	12.4	(0.1)	-30.5	(0.2)	-57.4	(0.8)	18.1	(0.1)	12.5	(0.0)	-30.6	(0.1)
	¹ H	-46.0	(0.4)	24.6	(0.1)	1.9	(0.1)	-26.5	(0.1)	-46.0	(0.4)	24.9	(0.2)	1.6	(0.3)	-26.5	(0.1)
	¹ H	-42.8	(0.2)	22.8	(0.1)	0.0	(0.1)	-22.8	(0.0)	-42.9	(0.3)	23.0	(0.1)	-0.5	(0.4)	-22.5	(0.3)
	¹ H	13.8	(0.1)	-5.4	(0.0)	-2.3	(0.1)	7.7	(0.1)	13.5	(0.1)	-5.4	(0.0)	-2.3	(0.1)	7.8	(0.1)
	¹⁷ O	-32.3	(1.1)	45.7	(0.1)	52.9	(0.4)	-98.6	(0.4)	-33.4	(0.1)	45.8	(0.0)	53.2	(0.0)	-99.0	(0.0)
O ₂ H	¹⁷ O	-56.6	(5.7)	124.3	(0.3)	125.6	(0.2)	-249.9	(0.5)	-59.6	(2.7)	124.1	(0.1)	125.5	(0.1)	-249.6	(0.2)
	¹ H	-23.8	(0.7)	31.5	(0.1)	-11.3	(0.0)	-20.3	(0.1)	-24.2	(0.2)	31.6	(0.1)	-11.3	(0.0)	-20.3	(0.0)
	¹⁷ O	-86.8	(2.7)	37.9	(0.1)	31.0	(0.2)	-68.8	(0.3)	-88.6	(0.9)	37.8	(0.0)	30.9	(0.1)	-68.7	(0.1)
CO ₂ ⁻	¹³ C	364.1	(0.4)	-44.7	(0.1)	-37.5	(0.5)	82.2	(0.5)	364.0	(0.4)	-44.7	(0.1)	-37.3	(0.2)	82.0	(0.3)
	¹⁴ N	24.0	(1.4)	-43.2	(0.1)	-44.1	(0.0)	87.3	(0.1)	24.6	(0.8)	-43.2	(0.0)	-44.2	(0.0)	87.3	(0.1)
NH ₂	¹ H	-65.6	(0.9)	62.1	(0.1)	-5.1	(0.1)	-57.0	(0.1)	-65.4	(0.6)	62.1	(0.1)	-5.1	(0.1)	-57.1	(0.0)
	¹⁴ N	146.7	(0.1)	-23.5	(0.1)	-19.8	(0.3)	43.3	(0.4)	146.5	(0.3)	-23.5	(0.1)	-19.6	(0.1)	43.0	(0.1)
NO ₂	¹⁷ O	-54.2	(1.9)	54.2	(2.2)	56.4	(2.2)	-110.6	(0.0)	-55.0	(1.0)	54.2	(2.2)	56.4	(2.3)	-110.6	(0.0)
	¹⁴ N	45.0	(2.1)	-48.8	(0.2)	-51.7	(0.1)	100.6	(0.3)	46.2	(1.0)	-48.7	(0.1)	-51.6	(0.0)	100.4	(0.1)
NF ₂	¹⁹ F	155.8	(7.0)	-194.8	(2.9)	-257.4	(1.0)	452.2	(3.9)	157.3	(5.6)	-196.6	(1.0)	-258.7	(0.2)	455.3	(0.8)
	¹⁴ N	93.8	(4.0)	-50.8	(0.3)	-50.8	(0.3)	101.6	(0.5)	96.1	(1.7)	-50.6	(0.1)	-50.6	(0.1)	101.2	(0.2)
NF ₃ ⁺	¹⁹ F	286.7	(17.9)	-342.6	(1.6)	-193.3	(2.9)	535.8	(4.4)	298.3	(6.3)	-344.4	(0.2)	-195.0	(1.1)	539.4	(0.9)
	¹⁷ O	-30.9	(1.5)	48.8	(0.2)	53.5	(0.0)	-102.3	(0.2)	-29.4	(3.0)	48.3	(0.8)	52.8	(0.6)	-101.1	(1.4)
O ₃ ⁻	¹⁷ O	-74.7	(5.8)	83.3	(0.4)	87.7	(0.1)	-171.1	(0.4)	-76.7	(3.8)	87.4	(4.4)	92.1	(4.4)	-179.5	(8.8)
	¹⁷ O	-29.5	(1.7)	58.3	(0.1)	58.6	(0.1)	-116.9	(0.0)	-30.0	(1.3)	58.2	(0.1)	58.8	(0.2)	-117.0	(0.1)
ClO ₂	¹⁷ O	-29.5	(1.7)	58.3	(0.1)	58.6	(0.1)	-116.9	(0.0)	-30.0	(1.3)	58.2	(0.1)	58.8	(0.2)	-117.0	(0.1)

	²⁵ Cl	39.3	(3.4)	-75.3	(0.1)	-79.9	(0.3)	155.2	(0.2)	40.9	(1.8)	-75.4	(0.2)	-79.9	(0.3)	155.3	(0.1)
MgF	²⁵ Mg	-311.7	(2.0)	3.9	(0.1)	3.9	(0.1)	-7.8	(0.1)	-313.2	(0.6)	3.9	(0.0)	3.9	(0.0)	-7.7	(0.0)
	¹⁹ F	189.3	(2.1)	-56.4	(2.2)	-56.4	(2.2)	112.9	(4.4)	189.5	(1.9)	-57.5	(1.1)	-57.5	(1.1)	115.0	(2.2)
SH ⁺	³² S	34.2	(0.5)	-97.7	(0.1)	48.9	(0.1)	48.9	(0.1)	33.9	(0.8)	-97.6	(0.1)	48.8	(0.0)	48.8	(0.0)
	¹ H	-52.6	(0.2)	22.6	(0.1)	-11.3	(0.1)	-11.3	(0.1)	-52.5	(0.2)	22.6	(0.1)	-11.3	(0.1)	-11.3	(0.1)
SO	³² S	13.1	(1.1)	31.9	(0.0)	31.9	(0.1)	-63.8	(0.1)	14.1	(0.2)	31.9	(0.0)	31.9	(0.0)	-63.7	(0.0)
	¹⁷ O	-38.5	(0.9)	63.2	(0.1)	-31.6	(0.1)	-31.6	(0.0)	-38.6	(0.7)	63.2	(0.0)	-31.6	(0.0)	-31.6	(0.0)
SiH ₃	²⁹ Si	-185.3	(0.8)	93.6	(0.1)	93.6	(0.0)	-187.3	(0.1)	-183.6	(0.8)	93.6	(0.0)	93.6	(0.0)	-187.1	(0.0)
	¹ H	-62.7	(0.2)	7.4	(0.1)	6.6	(0.1)	-14.0	(0.0)	-62.6	(0.1)	7.4	(0.1)	6.6	(0.1)	-14.0	(0.0)
S ₂	³² S	16.9	(1.0)	-52.0	(0.1)	26.0	(0.0)	26.0	(0.1)	17.7	(0.1)	-51.9	(0.0)	26.0	(0.0)	26.0	(0.0)
NH	¹⁴ N	15.3	(0.6)	-45.0	(0.1)	22.5	(0.0)	22.5	(0.0)	15.6	(0.3)	-45.0	(0.1)	22.5	(0.0)	22.5	(0.0)
	¹ H	-63.8	(0.7)	61.9	(0.0)	-30.9	(0.0)	-30.9	(0.0)	-63.7	(0.6)	61.9	(0.0)	-30.9	(0.0)	-30.9	(0.0)
OH ⁺	¹⁷ O	-43.3	(1.0)	159.2	(0.2)	-79.6	(0.1)	-79.6	(0.1)	-43.8	(0.6)	159.2	(0.2)	-79.6	(0.1)	-79.6	(0.1)
	¹ H	-72.1	(0.5)	86.5	(0.1)	-43.3	(0.0)	-43.3	(0.0)	-72.0	(0.4)	86.5	(0.1)	-43.3	(0.0)	-43.3	(0.0)
O ₂	¹⁷ O	-51.4	(1.4)	93.7	(0.2)	-46.9	(0.1)	-46.9	(0.1)	-52.2	(0.6)	93.6	(0.0)	-46.8	(0.0)	-46.8	(0.0)
CH ₂	¹³ C	253.7	(0.3)	-75.0	(0.1)	27.2	(0.0)	47.9	(0.1)	254.3	(0.8)	-75.0	(0.0)	27.2	(0.0)	47.8	(0.1)
	¹ H	-14.7	(0.4)	38.8	(0.0)	-15.2	(0.0)	-23.6	(0.1)	-14.8	(0.3)	38.8	(0.0)	-15.2	(0.0)	-23.5	(0.0)
AAE			2.2		0.3		0.2		0.4		1.0		0.2		0.2		0.3

TABLE IV: The DLPNO-based isotropic and anisotropic HFCCs in MHz on the *p*-benzoquinone radical anion in solvated in water in comparison with those obtained by various DFTs and the experimental values. The number of water molecules are indicated in the parenthesis. The def2-TZVPP basis set was used for all the calculations without frozen core.

		DLPNO-CCSD	B3LYP	CAM-B3LYP	PBE	M06-2X	B2PLYP	Exp.
Bridging Hydrogen (¹H)								
H ₂ O (× 4)	A _{aniso} (1)	-2.9	-3.0	-3.0	-2.9	-3.0	-2.9	-3.0
	A _{aniso} (2)	-3.1	-3.3	-3.3	-3.2	-3.3	-3.1	-3.0
	A _{aniso} (3)	6.0	6.3	6.3	6.1	6.3	6.0	6.0
	A _{iso}	0.5	0.2	0.3	-0.0	0.5	0.2	0.3
H ₂ O (× 20)	A _{aniso} (1)	-2.8	-2.9	-3.0	-2.9	-2.9	-2.8	-3.0
	A _{aniso} (2)	-3.2	-3.3	-3.3	-3.2	-3.3	-3.2	-3.0
	A _{aniso} (3)	6.0	6.3	6.3	6.1	6.2	6.0	6.0
	A _{iso}	0.3	-0.1	0.1	-0.3	0.2	-0.0	0.3
Carbonyl Oxygens (¹⁷O)								
H ₂ O (× 4)	A _{aniso} (1)	35.9	39.2	39.7	36.9	36.3	36.1	30.5
	A _{aniso} (2)	36.7	39.9	40.4	37.1	40.1	36.9	38.9
	A _{aniso} (3)	-72.6	-79.0	-80.1	-74.0	-76.4	-72.9	-69.5
	A _{iso}	-28.3	-22.3	-22.7	-13.0	-15.5	-23.4	-22.1
H ₂ O (× 20)	A _{aniso} (1)	34.6	38.0	38.4	36.0	35.3	35.3	30.5
	A _{aniso} (2)	35.5	38.8	39.2	36.3	39.0	36.0	38.9
	A _{aniso} (3)	-70.1	-76.8	-77.6	-72.3	-74.3	-71.3	-69.5
	A _{iso}	-27.7	-22.1	-22.4	-13.0	-14.5	-23.4	-22.1
Quinone Hydrogens (¹H)								
H ₂ O (× 4)	A _{aniso} (1)	-2.1	-2.3	-2.3	-2.1	-2.6	-2.2	-2.4
	A _{aniso} (2)	-3.7	-3.4	-3.4	-3.4	-3.2	-3.6	-3.5
	A _{aniso} (3)	5.8	5.7	5.7	5.6	5.8	5.8	5.9
	A _{iso}	-6.3	-5.7	-5.5	-5.7	-7.2	-6.3	-6.4
H ₂ O (× 20)	A _{aniso} (1)	-2.2	-2.3	-2.4	-2.2	-2.6	-2.3	-2.4
	A _{aniso} (2)	-3.7	-3.4	-3.4	-3.4	-3.4	-3.6	-3.5
	A _{aniso} (3)	5.9	5.7	5.8	5.6	6.0	5.9	5.9
	A _{iso}	-6.2	-5.6	-5.3	-5.5	-7.7	-6.2	-6.4

TABLE V: The first-order components in the HFCCs computed by the DLPNO-CCSD method and various commonly-used DFTs with the def2-TZVPP level of the basis set. For all the DFT calculations, the ZORA for relativistic correction and the ZORA-recontracted version of basis were used. The estimated sum of isotropic and anisotropic HFCCs was calculated by subtracting the scaled SOC contribution from the experimental value. Unless specifically indicated, the sign of the HFCCs is not known from the experiment.

		$A_{\text{total}}(1)$	$A_{\text{total}}(2)$	$A_{\text{total}}(3)$
$\text{V}(\text{H}_2\text{O})_6$	DLPNO-CCSD (Default1)	-226	-226	-227
	DLPNO-CCSD (Default2)	-228	-228	-228
	B3LYP	-179	-180	-180
	PBE	-184	-184	-185
	M06-2X	-40	-40	-40
	B2PLYP	-214	-214	-214
	CAM-B3LYP	-178	-178	-178
	Exp.	-247	-247	-247
$\text{VO}(\text{H}_2\text{O})_5$	DLPNO-CCSD (Default1)	-521	-222	-222
	DLPNO-CCSD (Default2)	-521	-222	-221
	B3LYP	-469	-167	-168
	PBE	-442	-154	-154
	M06-2X	-474	-165	-163
	B2PLYP	-579	-287	-281
	CAM-B3LYP	-471	-168	-167
	Exp.	-547	-212	-212
$\text{VO}(\text{acac})_2$	DLPNO-CCSD (Default1)	-491	-185	-174
	DLPNO-CCSD (Default2)	-492	-189	-177
	B3LYP	-246	-30	-20
	PBE	-407	-127	-110
	M06-2X	n.c.	n.c.	n.c.
	B2PLYP	-351	-67	-44
	CAM-B3LYP	-290	-30	-16
	Exp	520	190	190
$\text{Cr}(\text{H}_2\text{O})_6$	DLPNO-CCSD (Default1)	44	44	44
	DLPNO-CCSD (Default2)	44	44	44
	B3LYP	33	33	33
	PBE	32	33	33
	M06-2X	123	123	123
	B2PLYP	42	42	43
	CAM-B3LYP	33	33	33
	Exp.	55	55	55
$\text{Cr}(\text{N})(\text{CN})_5$	DLPNO-CCSD (Default1)	109	42	42
	DLPNO-CCSD (Default2)	106	39	39

	B3LYP	93	30	30
	PBE	80	18	18
	M06-2X	257	214	214
	B2PLYP	110	7	6
	CAM-B3LYP	95	37	37
	Exp.	107	42	42
Cr(N)(cyc)(NCCH₃)	DLPNO-CCSD (Default1)	126	53	54
	DLPNO-CCSD (Default2)	127	54	55
	B3LYP	116	44	43
	PBE	101	28	27
	M06-2X	306	255	255
	B2PLYP	n.c.	n.c.	n.c.
	CAM-B3LYP	122	52	51
	Exp.	115	44	44
Mn(H₂O)₆	DLPNO-CCSD (Default1)	-260	-260	-260
	DLPNO-CCSD (Default2)	-258	-258	-258
	B3LYP	-163	-163	-163
	PBE	-156	-156	-156
	M06-2X	-436	-436	-436
	B2PLYP	-220	-220	-220
	CAM-B3LYP	-165	-165	-165
	Exp.	-245	-245	-245
Mn(N)(cyc)(NCCH₃)	DLPNO-CCSD (Default1)	-559	-161	-160
	DLPNO-CCSD (Default2)	-545	-147	-145
	B3LYP	-461	-130	-128
	PBE	-433	-38	-35
	M06-2X	-1171	-916	-914
	B2PLYP	-586	158	144
	CAM-B3LYP	-462	-163	-160
	Exp.	560	180	180
Ni(H)(CO)₃	DLPNO-CCSD (Default1)	-77	101	102
	DLPNO-CCSD (Default2)	-73	104	104
	B3LYP	-95	78	79
	PBE	-89	64	65
	M06-2X	0	124	187
	B2PLYP	-95	106	106
	CAM-B3LYP	-97	85	86
	Exp.	-84	47	47
	Estimated A _{iso} +aniso	-83	67	67
Cu(NH₃)₄	DLPNO-CCSD (Default1)	-1020	-187	-189
	DLPNO-CCSD (Default2)	-1020	-194	-192

	B3LYP	-848	-103	-106
	PBE	-712	-63	-66
	M06-2X	-1001	-104	-113
	B2PLYP	-1039	-158	-162
	CAM-B3LYP	-885	-113	-117
	Exp.	586	71	71
	Estimated $A_{\text{iso}+\text{aniso}}$	940	142	142
Cu(acac)₂				
	DLPNO-CCSD (Default1)	-1061	-178	-179
	DLPNO-CCSD (Default2)	-1059	-184	-185
	B3LYP	-889	-113	-118
	PBE	-714	-76	-83
	M06-2X	-1190	-284	-287
	B2PLYP	-1084	-167	-164
	CAM-B3LYP	-931	-119	-115
	Exp.	-550	-60	-60
	Estimated $A_{\text{iso}+\text{aniso}}$	-975	-168	-158
Cu(en)₂				
	DLPNO-CCSD (Default1)	-1021	-200	-202
	DLPNO-CCSD (Default2)	-1023	-214	-212
	B3LYP	-853	-134	-134
	PBE	-704	-84	-84
	M06-2X	-1090	-219	-220
	B2PLYP	-1062	-194	-193
	CAM-B3LYP	-896	-146	-147
	Exp.	608	83	83
	Estimated $A_{\text{iso}+\text{aniso}}$	911	158	158
