

Beyond SCF Convergence: Robust Electronic-State Assessment of a Biological Dicopper QM Cluster

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Abstract

Accurate electronic-state assignment is essential for reliable quantum-mechanical modeling of multinuclear transition-metal sites, yet self-consistent-field (SCF) convergence alone does not establish physical comparability or orbital stability. Here, we reassess a 95-atom dicopper cluster derived from *Manduca sexta* prophenoloxidase using a validation strategy based on electron-count consistency, determinant identity, orbital stability, and methodological robustness. Reconstruction of the original calculations showed that two previously compared converged solutions had different total charges, invalidating their apparent energy difference for state ranking. Electron-count-consistent calculations for the $Q = +4$ cluster instead yielded broken-symmetry (BS) and high-spin triplet determinants that were effectively degenerate, retained opposite- and parallel-spin localization, respectively, and were independently confirmed as orbital-stable by electronic-Hessian analysis. The BS–triplet splitting remained below 0.4 cm^{-1} across integration grids, two quantum-chemistry programs, three hybrid functionals, three basis-set levels, and a low-dielectric continuum environment. Although the splitting varied with computational details, no calculation provided a meaningful separation sufficient for an unambiguous ground-state assignment. These results show that electronic-state assessment should precede energetic interpretation and explicitly verify electron count, determinant identity, orbital stability, and robustness to computational choices.

1. Introduction

Copper-containing proteins exploit the accessible redox chemistry and flexible coordination preferences of copper to support a wide range of biological processes, including oxygen activation, substrate oxidation, and electron-transfer chemistry [1]. Type-3 copper sites are particularly notable because they contain two electronically coupled copper ions coordinated predominantly by histidine ligands, and their properties depend on oxidation state, ligand environment, and spin coupling [1, 2]. The crystal structure of *Manduca sexta* prophenoloxidase provides a biologically relevant example of this architecture and reveals a canonical type-3 dicopper active site within an insect enzyme involved in innate immune chemistry [3].

Density functional theory (DFT) provides a practical Kohn-Sham framework for treating the electronic structure of molecules and materials [4], but assignment of an electronic state to multinuclear transition-metal centers remains nontrivial. Partially occupied d shells, closely spaced electronic configurations, spin polarization, and near-degeneracy can generate competing solutions whose relative properties depend on the exchange-correlation treatment, basis set, molecular environment, and orbital initialization [5, 6]. Spin-state energetics and magnetic exchange coupling are particularly sensitive observables in transition-metal DFT [5–7]. Systematic studies of dicopper models likewise show that changes in electronic-structure protocol, basis representation, and dielectric treatment can substantially affect calculated structures and electronic characteristics [8, 9]. Exchange-coupling predictions for Cu dimers also show pronounced method dependence, reinforcing the need for explicit validation when small state splittings are interpreted [10].

An additional complication is the distinction between self-consistent-field convergence and electronic-state stability. SCF convergence establishes that an iterative procedure has reached a self-consistent stationary solution, but it does not guarantee that the determinant is a local minimum with respect to allowed orbital rotations; formal stability analysis is a separate variational test [11]. Moreover, different starting orbitals or occupation patterns can converge to distinct SCF solutions of the same molecular problem [12]. Consequently, a converged determinant must be characterized beyond the convergence flag when competing electronic solutions are relevant. Energetic comparison also requires that the compared calculations represent the same molecular composition, total electron count, geometry, Hamiltonian, and numerical protocol. A failure at this bookkeeping level cannot be repaired by tighter SCF convergence or by subsequent population or orbital analysis.

Broken-symmetry (BS) approaches provide a practical single-determinant framework for spin-coupled multinuclear transition-metal systems [6, 13, 14]. In a BS determinant, alpha- and beta-spin densities are allowed to localize differently on interacting centers, intentionally breaking spin symmetry to represent open-shell or antiferromagnetically coupled character. Consequently, the expectation value of $\langle S^2 \rangle$ for a BS determinant should not be interpreted in the same manner as that of a nominally spin-pure restricted state [6, 14]. For two coupled spin-1/2 centers, an $M_S = 0$ BS determinant can possess an intermediate $\langle S^2 \rangle$ between the ideal singlet and triplet limits. Such a value alone is therefore insufficient to accept or reject the BS solution; spin topology, the corresponding high-spin state, orbital stability, and the robustness of the energetic relationship must be considered together.

This distinction becomes especially important when the energetic separation between alternative determinants is very small. Magnetic exchange couplings obtained from BS-DFT can be strongly dependent on the density functional and other methodological choices, and careful validation is therefore required before small calculated splittings are given physical significance [5–7]. For a dicopper model with a sub-wavenumber BS-high-spin separation, the scientifically useful question is not simply which determinant is numerically lower, but whether the near-degenerate relationship survives changes in numerical integration, electronic-structure implementation, density functional, basis set, and environmental polarization. Such robustness testing converts state assignment from a single-calculation decision into a reproducible electronic-structure assessment.

Here, we apply this strategy to a 95-atom QM cluster derived from the type-3 dicopper site of *Manduca sexta* prophenoloxidase. The study began with reconstruction and audit of historical calculations that had produced apparently distinct converged electronic solutions. This audit revealed that two previously compared energies corresponded to different total charge states and therefore could not constitute a valid electronic-state energy comparison. We subsequently established electron-count-consistent BS and high-spin reference determinants for the $Q = +4$ cluster and evaluated their relationship through progressively stricter numerical and methodological tests. These included integration-grid refinement, independent implementation in two quantum-chemistry programs, formal SCF stability analysis, variation of the hybrid density functional and basis set, and a low-dielectric continuum sensitivity calculation.

The objective is not to assign a universal ground state to biological dicopper centers, nor to propose a new electronic-structure method. Rather, this work uses a biological dicopper cluster as a case study to establish a practical hierarchy of checks that should precede energetic interpretation: electron-count consistency, electronic-state identity, orbital stability, and methodological robustness. The resulting workflow illustrates how calculations that are individually well converged can otherwise support qualitatively misleading conclusions when these conditions are not explicitly verified.

2. Materials and Methods

2.1. Dicopper QM cluster

The QM model was derived from the crystallographic structure of *Manduca sexta* prophenoloxidase (PDB ID: 3HHS) [3]. The present analysis focused on the PPO2 dicopper center. The first coordination sphere comprises six histidine residues, with His215, His219, and His245 associated with one Cu center and His368, His372, and His408 associated with the second Cu center.

The historical QM cluster was reconstructed without changing the atomic ordering or Cartesian coordinates used in the original calculations. The resulting model contained 95 atoms and consisted of the two Cu centers, six histidine-derived coordination fragments, and one explicit H₂O molecule associated with the dicopper site. Inspection of the complete coordinate set confirmed that the oxygen-containing species in the computational model was H₂O rather than an isolated oxide atom. The Cu-Cu distance in the fixed cluster geometry was 4.8588 Å, whereas the Cu1-O and Cu2-O distances were 2.6522 and 2.4842 Å, respectively.

All calculations reported in the present electronic-state validation were single-point calculations performed on this common 95-atom geometry. No geometry optimization was introduced during the validation workflow. This design was adopted deliberately so that changes in the electronic-state relationship could be attributed to electronic-structure or environmental variables rather than to simultaneous structural relaxation. The composition and key geometric features of the reconstructed QM cluster are shown in Fig. 1.

2.2. Reconstruction and electron-count audit of historical calculations

The original GAMESS input and output files were re-examined before performing new state comparisons. For each historical solution, the total molecular charge, spin multiplicity, restricted or unrestricted formalism, density functional, basis-set specification, orbital-restart instructions, and final SCF energy were independently identified from the corresponding calculation files.

The historical calculations employed B3LYP [15, 16] with the 6-31G(d) basis set [17, 18] in GAMESS [19], specified as GBASIS=N31, NGAUSS = 6, and NDFUNC = 1, without an effective core potential on Cu.

Reconstruction showed that the historical BS determinant with an energy near -5183.59 Eh was a $Q = +4$, $M_S = 0$ unrestricted solution, whereas the determinant previously treated as a lower-energy alternative was a $Q = +2$ closed-shell solution. Because the two calculations contained different numbers of electrons, their absolute SCF energies were not used for electronic-state ranking in the present study.

Throughout the revised workflow, relative electronic energies were compared only when molecular composition, total charge, geometry, electronic-structure method, basis set, and relevant numerical settings were identical. Cross-charge-state energy differences were treated solely as provenance information rather than as state splittings.

2.3. GAMESS baseline calculations

Baseline calculations were performed with GAMESS using B3LYP/6-31G(d) on the fixed 95-atom geometry. Four reference calculations were used to reconstruct the relevant electronic-state space: a $Q = +2$ restricted singlet used as a reconstruction control; a $Q = +4$ restricted singlet; a $Q = +4$ unrestricted BS $M_S = 0$ determinant; and a $Q = +4$ unrestricted high-spin triplet determinant. The unrestricted calculations were performed without molecular symmetry constraints. The BS determinant was generated from an unrestricted initial guess with spin mixing, whereas the triplet was obtained independently from a high-spin unrestricted calculation.

For the new baseline calculations, DIIS SCF convergence [20] was employed with a convergence threshold of 10^{-8} Eh and a maximum of 300 SCF iterations. The purpose of the $Q = +2$ calculation was to verify reconstruction of the historical closed-shell result; it was not included in energetic comparisons with the $Q = +4$ states.

2.4. Numerical integration-grid validation

The numerical robustness of the $Q = +4$ BS and triplet energy difference was evaluated in GAMESS using progressively denser DFT integration grids. Matching converged orbitals from the corresponding baseline electronic state were used as restart guesses. Two grids were examined, both using 96 radial points and Lebedev angular grids [21] containing either 590 or 1202 points; the corresponding inner-grid settings were kept consistent with the main grid. A tighter SCF convergence threshold of 10^{-9} Eh was applied. BS and triplet energies were always compared within the same integration grid; changes in absolute total energy between different grids were not interpreted as state splittings.

2.5. Independent ORCA calculations and BS construction

Independent electronic-state calculations were performed with ORCA 6.1.1 [22] using unrestricted Kohn-Sham DFT [4]. The B3LYP/6-31G(d) calculations employed RIJCOSX, whose chain-of-spheres exchange approximation is described by Neese et al. [23], together with DEFGRID3, VeryTightSCF, and TRAH-assisted SCF convergence. Strict convergence checking was enforced for the final reference solutions.

The high-spin $Q = +4$ triplet was converged first. The corresponding $M_S = 0$ BS determinant was then generated from the converged high-spin orbitals by reversing the spin density on one Cu center using the

ORCA FlipSpin procedure and specifying FinalMs 0 [22]. Constructing the BS solution from a converged high-spin reference is consistent with standard broken-symmetry exchange-coupling workflows [6]. This high-spin-to-BS construction was used systematically in subsequent ORCA calculations so that each BS determinant originated from the corresponding converged high-spin state at the same functional and basis set.

Absolute GAMESS and ORCA energies were not directly compared because implementation-specific differences, including basis-function conventions, can produce offsets in absolute total energies. Cross-program validation was instead based on electronic-state identity, spin localization, orbital stability, and the BS-triplet energy difference evaluated internally within each program.

2.6. Formal SCF stability analysis

Formal orbital-stability calculations were performed in ORCA for the converged $Q = +4$ BS and triplet determinants. SCF stability analysis examines the electronic Hessian with respect to orbital rotations and tests whether a converged stationary determinant is stable within the allowed variational space [11]. The unrestricted calculations used STABPerform true, automatic restarting from an unstable solution disabled, and three requested stability roots [22]. A determinant was considered orbital-stable when ORCA classified the wavefunction as stable and the calculated lowest electronic-Hessian eigenvalues were positive. Formal stability analysis was performed for the B3LYP/6-31G(d) reference determinants and repeated for both states at B3LYP/def2-TZVP.

2.7. Density-functional sensitivity

Functional sensitivity was evaluated at the fixed geometry using a common 6-31G(d) basis and otherwise consistent ORCA settings. Three hybrid functionals spanning different fractions of exact exchange were examined: TPSSh (approximately 10%) [24], B3LYP (20%) [15, 16], and PBE0 (25%) [25, 26]. This set was used as a controlled sensitivity scan rather than as a claim that any one functional provides a definitive benchmark for the dicopper state ordering. For each functional, the $Q = +4$ triplet determinant was converged first, followed by construction of the matching BS determinant from that same-functional triplet using the FlipSpin/FinalMs procedure. Energy differences were therefore evaluated only between states calculated with identical functional, basis set, geometry, integration grid, and molecular charge.

2.8. Basis-set sensitivity

Basis-set sensitivity was examined at the B3LYP level using 6-31G(d), def2-SVP, and def2-TZVP [27]. The geometry, charge, and electronic-state construction protocol were unchanged. When orbitals from a smaller basis were used to initialize a calculation in a larger basis, ORCA's F-matrix orbital-projection procedure (GuessMode FMatrix) was used. The converged triplet at each target basis was subsequently used to construct the corresponding BS determinant. Because Mulliken spin populations can depend on the basis set and population-analysis scheme, their absolute numerical values were not used for

quantitative cross-basis comparison [28]; they were used primarily to verify preservation of the expected state topology.

2.9. Low-dielectric continuum sensitivity

Environmental polarization was assessed with the conductor-like polarizable continuum model (C-PCM) [29] in ORCA at B3LYP/def2-TZVP. A dielectric constant of $\epsilon = 4.0$ and refractive index of 1.0 were used while retaining the fixed gas-phase cluster geometry. This calculation was designed as a low-dielectric sensitivity test rather than as a literal representation of a uniform protein dielectric environment. The electrostatic reaction field was included self-consistently during the SCF procedure. The triplet was converged first in the continuum, followed by construction and convergence of the matching BS determinant under identical C-PCM conditions. No high-dielectric continuum calculations were included in the final validation workflow.

2.10. Electronic-state characterization and energy analysis

Electronic-state identity was assessed using $\langle S^2 \rangle$ together with Mulliken atomic spin populations [30] at both Cu centers and at the oxygen atom of the explicit H₂O molecule. A valid triplet determinant was required to retain parallel Cu spin polarization and an $\langle S^2 \rangle$ value close to the expected high-spin value. The corresponding BS determinant was identified by opposite Cu spin polarization and an intermediate $\langle S^2 \rangle$, consistent with intentional spin-symmetry breaking in the BS formalism [6, 13, 14].

For each methodologically matched pair, the determinant energy difference was defined as

$$\Delta E = E_T - E_{BS}$$

where E_T and E_{BS} are the high-spin triplet and broken-symmetry electronic energies, respectively. For descriptive analysis of magnetic coupling, the approximate spin-projection expression commonly referred to as the Yamaguchi approach was used [31, 6]:

$$J = (E_{BS} - E_T) / (\langle S^2 \rangle_T - \langle S^2 \rangle_{BS})$$

with the spin-Hamiltonian convention $H = -2J \mathbf{S}_1 \cdot \mathbf{S}_2$, consistent with the convention used for the present Yamaguchi analysis [31, 6]. Under this convention, positive J corresponds to a high-spin-favoring sign. Because all calculated splittings were extremely small, neither the sign of J nor the sign of the raw determinant energy difference was used to claim an unambiguous physical ground state. Energy differences were converted using $1 \text{ Eh} = 627.509474 \text{ kcal mol}^{-1}$, $2625.499639 \text{ kJ mol}^{-1}$, and $219474.63137 \text{ cm}^{-1}$.

2.11. Reproducibility and treatment of interrupted calculations

Input files, converged orbital restart files, and principal electronic-structure outputs were retained for each validated calculation. Calculations interrupted before normal program termination were excluded

from numerical analysis. In particular, an interrupted TPSSh triplet calculation caused by an external power failure was archived for provenance, but its incomplete restart data were not reused; the calculation was repeated cleanly from the previously validated B3LYP triplet reference. Only normally terminated calculations with verified SCF convergence and preserved electronic-state identity were included in reported energetic comparisons.

2.12. Use of artificial intelligence tools

Generative artificial intelligence (ChatGPT, OpenAI) was used during manuscript preparation for organizational assistance, language refinement, and editorial drafting. The authors take full responsibility for the final content, scientific interpretation, and conclusions of the manuscript.

3. Results

3.1. Reconstruction of the historical electronic-state comparison

Re-examination of the historical GAMESS calculations revealed that the two electronic solutions previously interpreted as competing states did not correspond to the same total molecular charge. The BS calculation with a final energy of -5183.5878301957 Eh was a $Q = +4$, $M_S = 0$ unrestricted determinant, whereas the apparently lower-energy solution at -5184.4313209895 Eh was a $Q = +2$ closed-shell determinant. The previously reported energy difference of approximately 0.84349 Eh therefore reflected a change in total electron number rather than an electronic-state splitting within a common electron-number sector. Accordingly, this energy difference was excluded from all subsequent state-ranking analysis.

As an internal reconstruction control, the $Q = +2$ closed-shell calculation was repeated independently at the historical B3LYP/6-31G(d) level and reproduced the original energy to within 4×10^{-10} Eh. Similarly, the $Q = +4$ BS determinant was regenerated without relying on the historical reordered orbital file and reproduced the historical energy to the same numerical precision. These reconstructions established that the historical calculations themselves were reproducible while demonstrating that their original energetic comparison was not electron-count consistent. The audit therefore changed the central electronic-state question from selection between the historical $Q = +2$ and $Q = +4$ solutions to comparison of properly matched states within the $Q = +4$ manifold. The electron-count audit and the corrected matched-state comparison are summarized in Table 1 and Fig. 2.

Table 1
Electron-count audit and corrected state definition.

Calculation	Actual charge	Multiplicity	Energy (Eh)	Role in revised analysis
Historical closed-shell solution	+ 2	1	-5184.4313209895	Reconstruction control only
Historical Q = + 4 BS solution	+ 4	1	-5183.5878301957	Valid Q = + 4 BS provenance
Correct high-spin reference	+ 4	3	-5183.5878308513	Valid Q = + 4 triplet reference
<i>Note. Absolute energies from different charge states are reported solely for provenance and were not used to construct relative electronic-state energies.</i>				

3.2. Electron-count-consistent Q = + 4 BS and high-spin states

Three Q = + 4 reference determinants were examined at the fixed B3LYP/6-31G(d) geometry: a restricted singlet, an unrestricted BS $M_S = 0$ determinant, and an unrestricted high-spin triplet. The restricted singlet converged to -5183.5353533894 Eh. The BS determinant converged to -5183.5878301961 Eh with $\langle S^2 \rangle = 1.008$, whereas the triplet converged to -5183.5878308513 Eh with $\langle S^2 \rangle = 2.008$.

The restricted singlet was higher than the BS determinant by 0.05247681 Eh, corresponding to approximately 32.93 kcal mol⁻¹. In contrast, the triplet and BS determinants differed by only -6.552×10^{-7} Eh, or -0.14380 cm⁻¹. The two unrestricted determinants displayed the expected distinct spin topologies. In the BS solution, the Cu centers carried opposite Mulliken spin populations of approximately + 0.716 and - 0.741, whereas the corresponding triplet displayed parallel Cu spin populations of approximately + 0.716 and + 0.740. The oxygen atom of the explicit H₂O molecule carried negligible spin density in both cases. These data identify two internally distinct but nearly isoenergetic Q = + 4 determinants. The intermediate $\langle S^2 \rangle$ of the BS determinant was therefore interpreted as a consequence of intentional spin-symmetry breaking rather than, by itself, as evidence that the determinant should be rejected.

3.3. The BS-triplet near-degeneracy is insensitive to integration-grid refinement

Because the BS-triplet separation was substantially smaller than typical electronic-structure energy scales, its sensitivity to numerical integration was evaluated using two denser DFT grids. With the 96 × 590 grid, the BS and triplet energies were - 5183.5883831588 and - 5183.5883838151 Eh, respectively, giving $\Delta E = -0.14404$ cm⁻¹. Increasing the angular grid to 1202 Lebedev points produced absolute energies of -5183.5883464403 Eh for the BS determinant and - 5183.5883470972 Eh for the triplet, corresponding to $\Delta E = -0.14417$ cm⁻¹.

The absolute BS energy shifted by approximately 8.06 cm⁻¹ between the two grids, more than fifty times larger than the BS-triplet splitting itself. Nevertheless, because both states were evaluated on identical grids, their relative separation changed by only about 1.3 × 10⁻⁴ cm⁻¹. Thus, the absolute DFT energy was measurably grid dependent, whereas the matched BS-triplet difference was numerically stable. This observation further emphasizes that sub-wavenumber state splittings should only be interpreted when both determinants are evaluated under strictly identical numerical conditions. This contrast is highlighted graphically in Fig. 4.

3.4. Independent ORCA calculations confirm two orbital-stable determinants

To determine whether the near-degenerate solutions reflected program-specific SCF behavior, the Q = + 4 states were independently reconstructed in ORCA. The strict B3LYP/6-31G(d) triplet exhibited $\langle S^2 \rangle$ = 2.007843 and parallel Cu spin populations of + 0.7111 and + 0.7368. Generation of the BS determinant from the converged high-spin orbitals produced an M_S = 0 solution with $\langle S^2 \rangle$ = 1.007852 and opposite Cu spin populations of approximately - 0.7115 and + 0.7371.

Formal electronic-Hessian stability analysis classified both determinants as stable SCF solutions. For the triplet, the three lowest calculated stability eigenvalues were 0.262031, 0.268504, and 0.271403 Eh, all positive. ORCA likewise explicitly classified the BS determinant as stable. Using the final stability-validated energies, E_T = -5183.538962738653 Eh and E_{BS} = -5183.538962052571 Eh, the ORCA BS-triplet separation was - 0.15058 cm⁻¹. The corresponding approximate Yamaguchi exchange parameter was + 0.15058 cm⁻¹ under the adopted Hamiltonian convention. The close agreement with the GAMESS result demonstrates that the near-degeneracy is not attributable to a single SCF implementation. More importantly, formal stability testing shows that neither determinant is an electronically unstable stationary solution within the tested orbital-rotation space. The key state-identity and stability diagnostics at the two formally tested ORCA levels are summarized in Table 2. The corresponding BS and triplet spin topologies and their orbital-stability characteristics are illustrated in Fig. 3.

Table 2
Electronic-state identity and orbital stability of the validated Q = + 4 determinants.

Level	State	$\langle S^2 \rangle$	Cu1 spin	Cu2 spin	Stability
ORCA B3LYP/6-31G(d)	BS	1.007852	-0.7115	+ 0.7371	Stable
ORCA B3LYP/6-31G(d)	Triplet	2.007843	+ 0.7111	+ 0.7368	Stable
ORCA B3LYP/def2-TZVP	BS	1.011059	-0.5394	+ 0.5747	Stable
ORCA B3LYP/def2-TZVP	Triplet	2.011051	+ 0.5391	+ 0.5746	Stable
<i>Note. Opposite Cu spin signs identify the BS determinant, whereas parallel Cu spin signs identify the high-spin triplet. Full Mulliken populations and stability-Hessian diagnostics are provided in the Supporting Information.</i>					

3.5. Functional variation changes the magnitude but not the near-degenerate regime

The robustness of the BS-triplet relationship to exchange-correlation treatment was evaluated using TPSSh, B3LYP, and PBE0 with a common 6-31G(d) basis and otherwise matched ORCA settings. All three functionals generated recognizable high-spin and BS determinants with the expected parallel and antiparallel Cu spin patterns. The determinant splittings were -0.18750 cm^{-1} for TPSSh, -0.15058 cm^{-1} for B3LYP, and -0.02135 cm^{-1} for PBE0. Thus, the magnitude showed clear functional dependence, decreasing substantially at PBE0, but all values remained well below 1 cm^{-1} . The corresponding Yamaguchi parameters were approximately $+0.18750$, $+0.15058$, and $+0.02135\text{ cm}^{-1}$. Although all three had the same formal high-spin-favoring sign under the chosen Hamiltonian convention, their extremely small magnitude argues against using the sign alone to assign an unambiguous physical ground state.

3.6. Basis-set enlargement preserves near-degeneracy

Basis-set sensitivity was evaluated at B3LYP using 6-31G(d), def2-SVP, and def2-TZVP. At def2-SVP, the triplet and BS determinants had $\langle S^2 \rangle$ values of 2.009888 and 1.009897, respectively, and $\Delta E = -0.36548\text{ cm}^{-1}$. At def2-TZVP, the triplet and BS determinants converged to -5184.840863131343 and -5184.840861334723 Eh, with $\langle S^2 \rangle$ values of 2.011051 and 1.011059; the corresponding splitting was -0.39431 cm^{-1} .

Formal stability analysis at def2-TZVP confirmed that both states remained orbital-stable. The three lowest stability eigenvalues were 0.259729, 0.264326, and 0.267753 Eh for the BS determinant and 0.259723, 0.264323, and 0.267691 Eh for the triplet. Although the calculated splitting increased relative to 6-31G(d), all basis sets retained the same central feature: the two unrestricted determinants remained separated by substantially less than 1 cm^{-1} . Because Mulliken populations vary strongly with basis representation, changes in their absolute numerical values were not interpreted as quantitative measures of charge or spin transfer across the basis-set series.

3.7. A low-dielectric reaction field reduces the splitting without removing near-degeneracy

Environmental polarization was evaluated at B3LYP/def2-TZVP using C-PCM with $\epsilon = 4.0$. The continuum-phase triplet converged to -5185.394208070818 Eh with $\langle S^2 \rangle = 2.006691$ and parallel Cu spin populations of $+0.6740$ and $+0.6929$. The corresponding BS determinant converged to -5185.394207227659 Eh with $\langle S^2 \rangle = 1.006700$ and antiparallel Cu spin populations of -0.6742 and $+0.6929$. The resulting splitting was -0.18505 cm^{-1} , corresponding to an approximate $J = +0.18505\text{ cm}^{-1}$.

Relative to the gas-phase B3LYP/def2-TZVP result of -0.39431 cm^{-1} , the low-dielectric continuum reduced the magnitude of the determinant separation by approximately 53%. Thus, environmental polarization had a measurable influence on the numerical coupling estimate but did not alter the central

qualitative conclusion: the BS and triplet determinants remained effectively degenerate on the scale of electronic-structure uncertainty.

3.8. Integrated robustness of the $Q = +4$ electronic-state relationship

Across all valid, electron-count-consistent comparisons performed in this study, the BS-triplet determinant separation remained between approximately -0.02 and -0.40 cm^{-1} . The relationship survived numerical integration-grid refinement, independent reconstruction in GAMESS and ORCA, formal orbital-stability analysis, variation among TPSSh, B3LYP, and PBE0, enlargement from 6-31G(d) to def2-TZVP, and introduction of a low-dielectric reaction field. No valid calculation produced a BS-triplet separation approaching even 1 cm^{-1} . Accordingly, although the triplet determinant was numerically lower in every matched comparison reported here, the magnitude of this preference is too small to justify an unambiguous ground-state assignment. The principal result is therefore not the sign of an individual energy difference, but the persistence of an effectively degenerate BS/high-spin manifold across multiple independent numerical and methodological perturbations. The complete set of validated matched splittings is summarized in Table 3 and Fig. 4.

Table 3
Summary of validated BS-triplet splittings.

Validation	Level/condition	$\Delta E = E_T - E_{BS}$ (cm^{-1})	Principal conclusion
Baseline	GAMESS B3LYP/6-31G(d)	-0.14380	Near-degenerate
Grid	96×590	-0.14404	Numerically robust
Grid	96×1202	-0.14417	Numerically robust
Program / stability	ORCA B3LYP/6-31G(d)	-0.15058	Both states stable
Functional	TPSSh/6-31G(d)	-0.18750	Near-degenerate
Functional	PBE0/6-31G(d)	-0.02135	Near-degenerate
Basis	B3LYP/def2-SVP	-0.36548	Near-degenerate
Basis / stability	B3LYP/def2-TZVP	-0.39431	Both states stable
Environment	B3LYP/def2-TZVP, C-PCM $\epsilon = 4$	-0.18505	Near-degenerate

4. Discussion

4.1. Electron-count consistency precedes electronic-state ranking

The most consequential result of the present reassessment was not the identification of a lower-energy determinant, but the recognition that the historical energy comparison did not involve a common electron count. The previously contrasted solutions belonged to different total charge states, $Q = +4$ and $Q = +2$, and their large absolute energy difference therefore could not represent an electronic-state splitting. This distinction is elementary in principle but important in practice. Electronic-structure calculations can possess multiple SCF stationary solutions associated with different orbital occupations or symmetry patterns [12], and convergence to one of them does not by itself establish variational stability [11]. Under workflows involving orbital restarts, alternative multiplicities, and occupation manipulations, meaningful energetic ranking therefore requires explicit control of molecular composition, electron number, geometry, electronic Hamiltonian, and numerical conditions before an energy difference is interpreted.

The reconstruction performed here illustrates why provenance and electron-count checks should occur at the beginning of an electronic-state assessment rather than after detailed orbital or population analyses. No degree of SCF convergence, spin analysis, or chemical interpretation can convert energies from different electron-number sectors into a valid state splitting. The historical closed-shell $Q = +2$ solution remains a reproducible quantum-chemical calculation, but it is not a competing electronic state of the $Q = +4$ manifold. Once this distinction is imposed, the relevant $Q = +4$ comparison becomes the relationship among the restricted singlet, BS determinant, and high-spin triplet.

4.2. An intermediate $\langle S^2 \rangle$ is not sufficient to reject a BS determinant

The original interpretation also treated the $\langle S^2 \rangle$ value of approximately 1.008 for the $M_S = 0$ determinant primarily as evidence of undesirable spin contamination. Such an interpretation is incomplete for a deliberately broken-symmetry wavefunction. In the BS framework for magnetically coupled transition-metal systems, the determinant is intentionally allowed to break spin symmetry so that opposite local spin polarization can be represented within a single-determinant formalism [6, 13, 14]. The resulting determinant is not expected to be an eigenfunction of S^2 . Consequently, an intermediate $\langle S^2 \rangle$ is characteristic of the mixed-spin determinant and cannot, by itself, establish that the SCF solution is physically inappropriate.

The present calculations provide several independent checks of this interpretation. First, the $M_S = 0$ determinant showed the expected antiparallel localization of spin density on the two Cu centers, whereas the high-spin determinant showed parallel Cu spin localization. Second, both states were reproducibly obtained using independent electronic-structure programs. Third, formal electronic-Hessian analysis classified both the BS and triplet determinants as orbital-stable solutions. The distinction between spin purity and orbital stability is therefore central: stability analysis addresses the local variational character of the SCF stationary point, not whether the determinant is an eigenfunction of S^2 [11]. For electronic-state assessment, $\langle S^2 \rangle$ should therefore be interpreted together with local spin

topology, the corresponding high-spin determinant, and formal stability information rather than used as an isolated accept/reject criterion.

4.3. The robust result is near-degeneracy, not a definitive triplet ground state

Every valid matched comparison in the present study placed the high-spin determinant numerically below the BS determinant. Taken in isolation, this repeated sign might appear to support a triplet ground-state assignment. The magnitude of the effect, however, leads to a different and more cautious conclusion. Across the complete validation set, the calculated BS-triplet separation ranged only from approximately 0.02 to 0.40 cm^{-1} . These values remained below 1 cm^{-1} despite substantial changes in integration grid, quantum-chemistry program, density functional, basis set, and dielectric treatment.

The important observation is therefore not that one determinant was consistently lower by a minute numerical amount, but that no tested perturbation produced a substantial energetic separation between the two orbital-stable solutions. Indeed, the magnitude of the calculated splitting changed several-fold across the functional and basis-set scans while remaining extremely close to zero. This distinction is particularly important in transition-metal DFT, where spin-state energetics and magnetic exchange interactions show appreciable dependence on the exchange-correlation treatment and computational protocol [5–7]. The present results accordingly do not support interpreting the sign of a fraction-of-a-wavenumber DFT energy difference as a definitive physical ground-state assignment. A more defensible description is that the fixed $Q = +4$ dicopper cluster possesses an effectively near-degenerate BS/high-spin determinant manifold at the DFT levels examined here.

4.4. Numerical and methodological perturbations provide complementary information

The successive validation stages were designed to answer different questions rather than to accumulate additional calculations indiscriminately. Integration-grid refinement addressed whether the minute BS-triplet gap was a numerical integration artifact. Although the absolute total energies changed noticeably when the angular grid was enlarged, the matched splitting remained essentially unchanged. Independent reconstruction in ORCA addressed whether the state relationship reflected program-specific SCF behavior. Agreement between GAMESS and ORCA at the level of determinant identity and BS-triplet separation, together with the subsequent stability tests, substantially reduces this possibility.

Variation of the density functional produced a larger effect on the magnitude of the splitting. TPSSh, B3LYP, and PBE0 all retained the same near-degenerate regime, but PBE0 reduced the calculated gap to only approximately 0.02 cm^{-1} . This sensitivity is consistent with the broader challenge of describing spin states and magnetic exchange in transition-metal systems using approximate density functionals [5–7]. Studies focused on dicopper systems likewise show that predicted electronic structure can respond appreciably to functional, basis-set, and dielectric choices [8, 9], while benchmark work on Cu dimers emphasizes substantial method dependence in calculated exchange coupling [10].

Basis-set enlargement from 6-31G(d) to def2-SVP and def2-TZVP increased the numerical separation, but the gap remained below 0.4 cm⁻¹. Explicit stability analysis at def2-TZVP confirmed that both determinants remained orbital-stable at the largest basis level examined. The low-dielectric C-PCM calculation provided a conceptually distinct sensitivity test: environmental polarization reduced the B3LYP/def2-TZVP splitting from approximately 0.39 to 0.19 cm⁻¹ without changing the identity of either determinant. Together, these tests show that robustness should not be defined as numerical invariance of a tiny energy difference. Instead, robustness in the present context means preservation of the same physical regime—two recognizable, stable, effectively degenerate determinants—under multiple independent perturbations of the computational protocol.

4.5. Implications for electronic-state workflows in metalloprotein modeling

The results suggest a hierarchical electronic-state assessment strategy for multinuclear transition-metal QM models. The first requirement is model identity: atomic composition, molecular charge, electron count, geometry, and computational Hamiltonian must be explicitly verified. Only after this condition is satisfied should alternative SCF solutions be compared energetically. The second requirement is determinant identity. Spin expectation values should be interpreted together with local spin densities and the intended multiplicity or BS topology. In particular, a mixed-spin BS determinant should not be rejected merely because its $\langle S^2 \rangle$ differs from the value expected for a spin-pure singlet, because spin-symmetry breaking is intrinsic to the BS construction [6, 13, 14].

The third requirement is electronic stability. When competing unrestricted solutions are central to the interpretation, formal orbital-stability analysis provides information that ordinary SCF convergence does not [11]. The fourth requirement is robustness. If an electronic-state conclusion depends on an extremely small energy difference, its persistence should be tested against the principal numerical and methodological choices relevant to the system; exchange-coupling calculations are known to be sensitive to functional and basis-set choices [6, 7]. The appropriate extent of such testing should therefore be proportional to the claim being made: a sub-wavenumber ground-state assignment requires stronger evidence than recognition of two effectively degenerate determinants.

This hierarchy has practical relevance before QM information is propagated into larger computational workflows. QM/MM calculations use a quantum description of the active region embedded in a larger molecular-mechanical environment, so assumptions made in the initial QM model can influence subsequent structural and energetic interpretation [32, 33]. Likewise, metal-center parameterization workflows explicitly use QM-derived information to construct molecular-mechanical models [34]. Establishing the electronic-state relationship before such transfer therefore provides a useful upstream quality-control step. Importantly, the present study does not suggest that every metalloprotein calculation requires the full sequence of grid, functional, basis, program, and stability tests performed here. Rather, additional calculations are warranted when they address a specific unresolved source of

electronic-state ambiguity, whereas redundant variations that do not alter the scientific inference provide diminishing returns.

4.6. Scope and limitations

Several limitations define the appropriate scope of the present conclusions. First, the calculations were performed on a single 95-atom cluster extracted from one biological dicopper site. The results therefore establish the electronic-state behavior of this model and demonstrate the utility of the assessment strategy, but they do not establish that all biological dicopper sites exhibit the same near-degenerate electronic structure.

Second, the geometry was held fixed throughout the validation workflow. This was advantageous for isolating electronic and methodological effects, but possible state-specific structural relaxation was not explored. The present conclusions therefore apply to the electronic-state landscape of the chosen cluster geometry rather than to fully relaxed free-energy surfaces.

Third, the protein environment was represented only through a low-dielectric continuum sensitivity calculation. Explicit protein environments can contribute electrostatic, steric, hydrogen-bonding, and conformational effects that are not represented by a uniform continuum model, which is one reason QM/MM treatments of proteins require careful definition of the QM region and its surroundings [32, 33]. The C-PCM result should consequently be interpreted as evidence that environmental polarization can affect the magnitude of the splitting, not as a quantitative model of the full protein environment.

Fourth, the study was designed around DFT-based determinant assessment rather than a definitive multireference benchmark. Spin-state energetics and magnetic exchange couplings are among the transition-metal properties for which DFT performance can be strongly method dependent [5–7], and benchmark studies of Cu dimers show that quantitatively reliable exchange coupling remains challenging even when more elaborate wavefunction-based approaches are considered [10]. Accordingly, a quantitatively rigorous magnetic coupling constant would require a different level of validation if such a value were the primary scientific target. In the present work, however, the objective is more limited: to determine whether routine SCF convergence is sufficient for electronic-state assignment and whether the competing determinants remain identifiable and stable under practical computational perturbations.

Finally, no direct experimental magnetic or spectroscopic observable was used to discriminate between the near-degenerate states. Future comparison with appropriate spectroscopic measurements, explicit protein-environment calculations, or an independent biological dicopper system would provide additional tests of the broader transferability of the workflow. Within these boundaries, the central conclusion is well supported: the electronic-state relationship of the present dicopper QM cluster cannot be reduced to the first converged SCF solution or to the sign of a minute determinant energy difference.

5. Conclusions

Reassessment of a 95-atom QM cluster derived from the type-3 dicopper center of *Manduca sexta* prophenoloxidase demonstrates that SCF convergence alone is insufficient for reliable electronic-state interpretation. The first critical finding was that two historically compared converged solutions belonged to different molecular charge states. Their large apparent energy difference was therefore not a valid electronic-state splitting. Once electron-count consistency was enforced within the $Q = +4$ manifold, the relevant BS and high-spin triplet determinants were found to be effectively degenerate.

Both determinants exhibited the expected local spin topology and were independently reproduced in two quantum-chemistry programs. Formal electronic-Hessian analysis further established that both were orbital-stable SCF solutions. Their energy separation remained below approximately 0.4 cm^{-1} across numerical-grid refinement, TPSSH/B3LYP/PBE0 functional variation, basis-set enlargement through def2-TZVP, and a low-dielectric continuum environment.

Although the triplet determinant was numerically lower in the matched calculations, the exceptionally small and method-dependent separation does not justify an unambiguous ground-state assignment. The robust result is instead the persistence of an effectively near-degenerate BS/high-spin manifold. The present case study therefore supports a hierarchical electronic-state assessment in which electron count and model identity are verified first, followed by determinant characterization, orbital-stability testing, and targeted robustness analysis before small energy differences are given chemical significance. SCF convergence should consequently be regarded as the beginning of electronic-state validation rather than its endpoint.

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Figures

Manduca sexta PPO2 active-site region

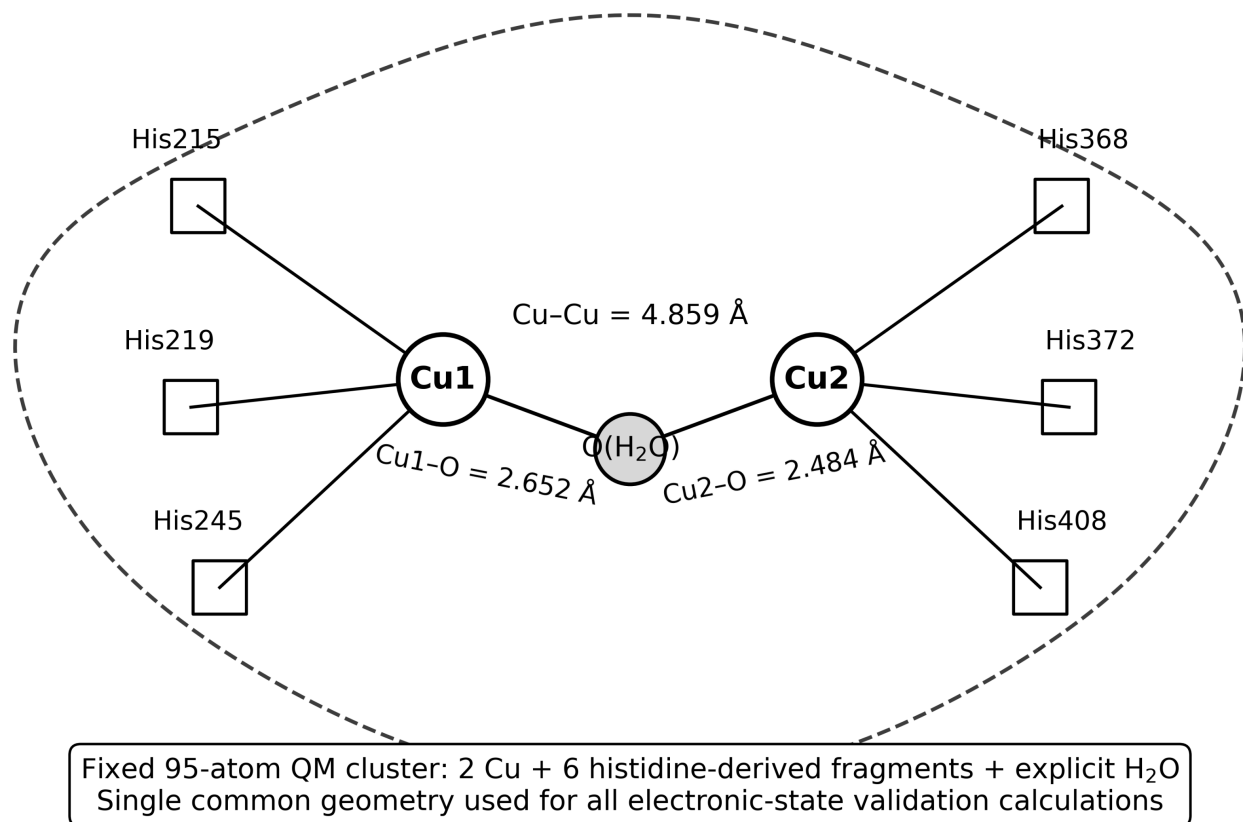
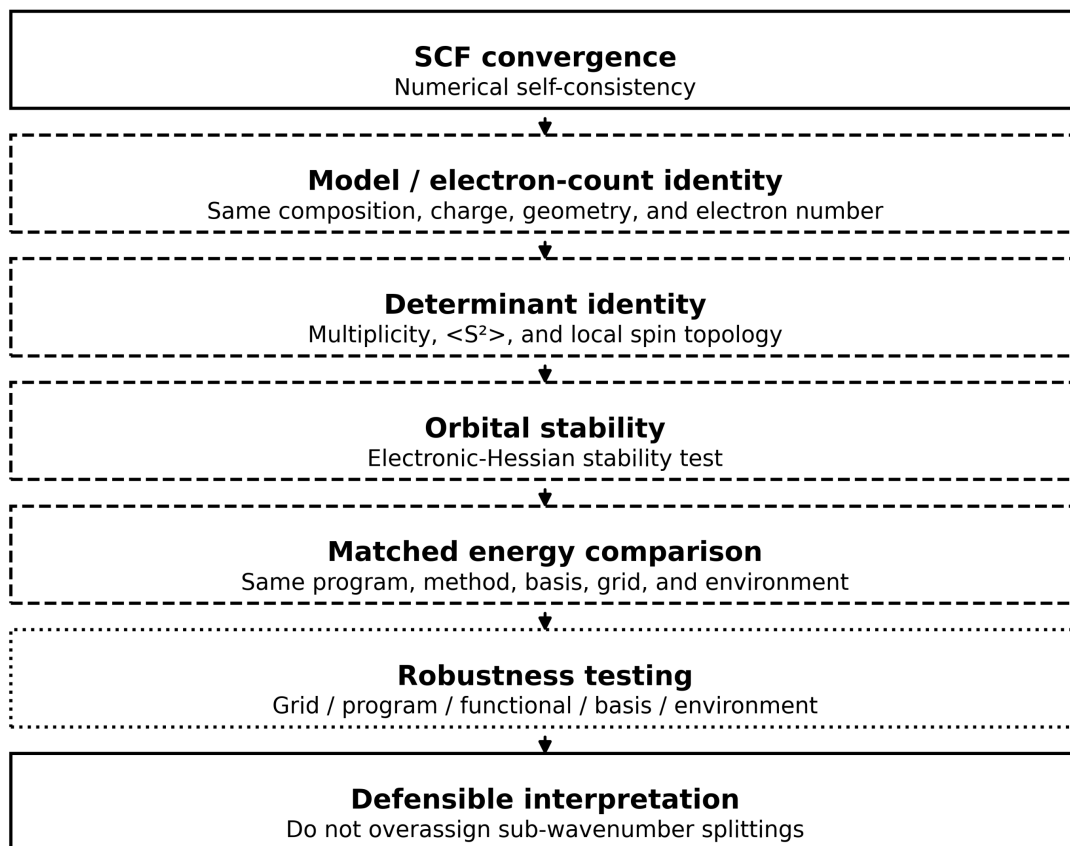


Figure 1

Schematic biological origin and definition of the dicopper QM cluster. The 95-atom model contains two Cu centers, six histidine-derived fragments, and one explicit H₂O molecule. Selected distances are shown. The same fixed geometry was used for all electronic-state validation calculations.

A**Electronic-state validation hierarchy****B****Historical comparison**

BS determinant
 $Q = +4$, $M_S = 0$
 $E = -5183.587830 \text{ Eh}$

✖ **INVALID: different electron counts**

Closed-shell determinant
 $Q = +2$, $M = 1$
 $E = -5184.431321 \text{ Eh}$

Corrected matched comparison

BS determinant
 $Q = +4$, $M_S = 0$
 $E = -5183.587830196 \text{ Eh}$

✖ **VALID: $\Delta E(\text{T-BS}) \approx -0.144 \text{ cm}^{-1}$**

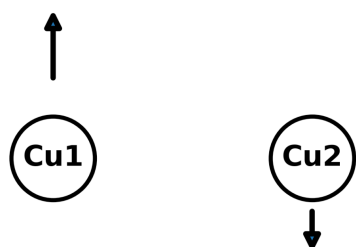
Triplet determinant
 $Q = +4$, $M = 3$
 $E = -5183.587830851 \text{ Eh}$

Different-charge absolute energies are provenance information only; they do not define an electronic-state splitting.

Figure 2

Electronic-state validation hierarchy and electron-count audit. (A) The workflow separates numerical SCF convergence from subsequent checks of model/electron-count identity, determinant identity, orbital stability, matched energetic comparison, and targeted robustness testing before chemical interpretation. (B) The historical $Q = +4$ BS and $Q = +2$ closed-shell energies cannot be ranked as competing electronic states because they contain different numbers of electrons. The corrected $Q = +4$ BS-triplet comparison gives $\Delta E(\text{T-BS}) \approx -0.144 \text{ cm}^{-1}$ at B3LYP/6-31G(d).

Broken-symmetry determinant



Antiparallel Cu spin localization

$$\langle S^2 \rangle \approx 1.01$$

ORCA stability: STABLE

def2-TZVP lowest Hessian roots:
0.259729, 0.264326, 0.267753 Eh

High-spin triplet determinant



Parallel Cu spin localization

$$\langle S^2 \rangle \approx 2.01$$

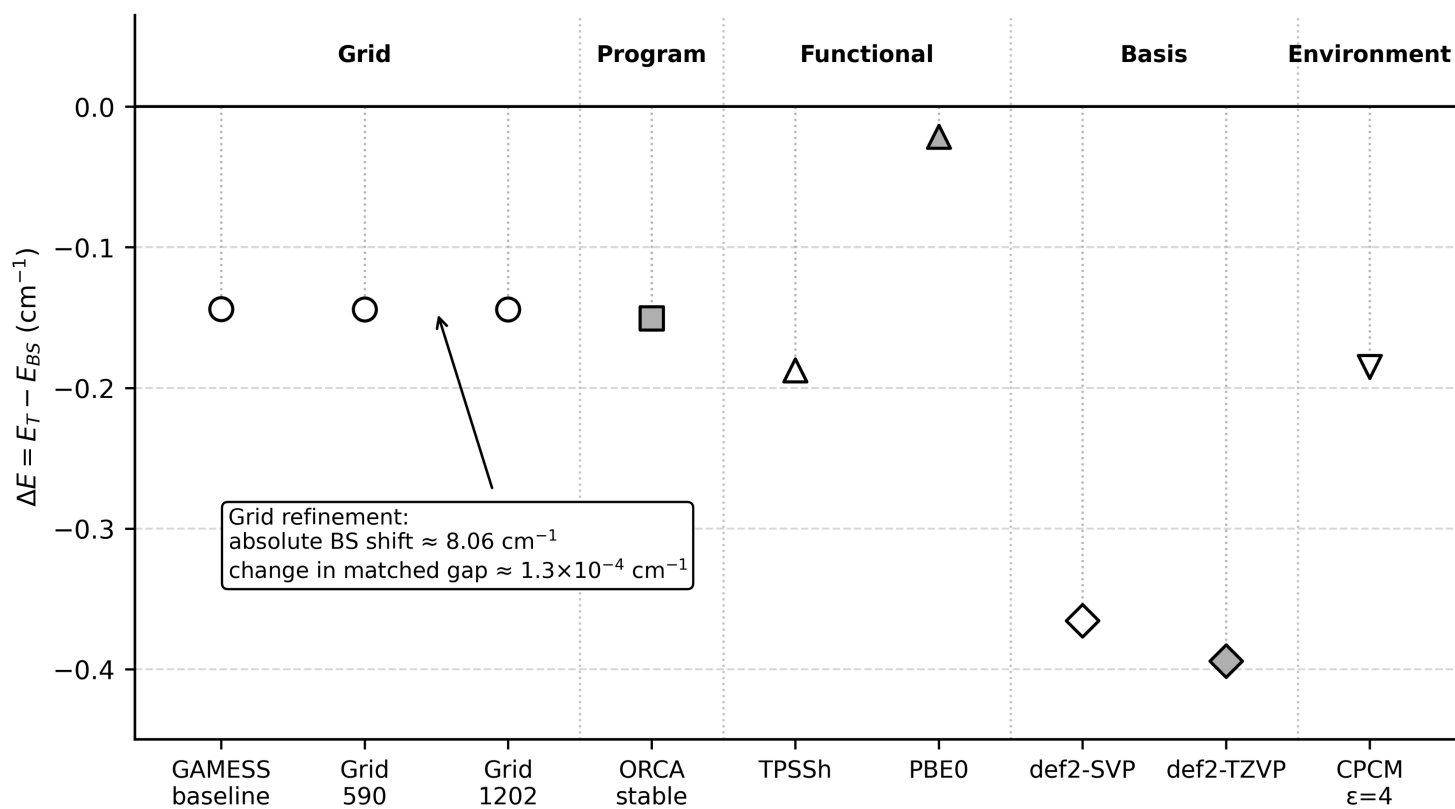
ORCA stability: STABLE

def2-TZVP lowest Hessian roots:
0.259723, 0.264323, 0.267691 Eh

Both determinants are recognizable, independently converged, and orbital-stable.

Figure 3

Electronic-state identity and orbital stability of the matched $Q = +4$ determinants. The BS solution retains antiparallel Cu spin polarization and $\langle S^2 \rangle \approx 1$, whereas the triplet retains parallel spin polarization and $\langle S^2 \rangle \approx 2$. Both states are orbital-stable in ORCA. The def2-TZVP stability roots shown are all positive.



All validated splittings remain below 0.4 cm^{-1} in magnitude.

Figure 4

Robustness of the BS-triplet determinant splitting to numerical, methodological, and environmental perturbations. The horizontal zero line denotes exact determinant degeneracy. All validated values remain between approximately -0.02 and -0.40 cm^{-1} . The grid-refinement callout highlights that the absolute BS energy shifts by approximately 8.06 cm^{-1} between the tested grids, whereas the matched BS-triplet gap changes by only approximately $1.3 \times 10^{-4} \text{ cm}^{-1}$. The B3LYP functional reference is represented by the stability-validated ORCA point and is not duplicated as a second functional-scan point.