

# QUANTUM COHERENCE IN PHOTOSYNTHETIC ANTENNA COMPLEXES: A REASSESSMENT OF “WARM AND WET” QUANTUM BIOLOGY AND THE PCFRI FUNCTIONAL-RELEVANCE FRAMEWORK

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**Abstract:** The two-decade arc of quantum-biology research on photosynthetic energy transfer has, over 2016–2023, undergone a substantial empirical and theoretical reassessment. The 2007 Engel et al. *Nature* observation of long-lived coherent oscillations in the Fenna–Matthews–Olson (FMO) complex at 77 K, followed by the Panitchayangkoon et al. (2010) demonstration that comparable oscillations persisted at physiological temperatures (277 K), generated the influential “warm and wet” hypothesis: that photosynthetic light-harvesting complexes exploit long-lived electronic quantum coherence to achieve near-unity energy-transfer efficiency, operating outside the conventional thermal-noise regime where decoherence should rapidly destroy electronic superpositions. The subsequent reassessment — anchored by Duan et al. (2017), who showed that electronic decoherence in FMO occurs within 60 fs at physiological temperatures, Thyraug et al. (2018a), and the Cao et al. (2020) 18-author consensus review “Quantum biology revisited” — has shifted the working consensus toward the interpretation that the long-lived oscillations originally attributed to electronic coherence are dominated by impulsively excited vibrational coherences rather than functionally relevant electronic superpositions. Wilkins & Dattani (2020) further argue that even if some inter-exciton coherences persist, they do not measurably enhance energy-transfer efficiency above incoherent Förster-type predictions. The Mirkovic et al. (2017) comprehensive review provides the framework against which the post-2016 reassessment is interpreted. The principal aim of this article is to formalise the cross-claim evaluation of the surviving quantum-coherence proposals through the Photosynthetic Coherence Functional Relevance Index (PCFRI), a normalised composite metric bounded on [0,1] that integrates five evaluative dimensions — spectroscopic detection robustness, origin specificity, decoherence-vs-energy-transfer timescale ratio, functional-role demonstration, and in-vivo relevance gap — and returns a quantitative ranking of competing claims. Applied to five canonical claim categories, PCFRI returns values in the 0.15–0.50 range, indicating that no current quantum-coherence proposal achieves the “demonstrated functional relevance” tier and that the post-2016 reassessment has, on the PCFRI calibration, empirically vindicated the sceptical position of Wilkins & Dattani (2020).

**Keywords:** *quantum biology, photosynthesis, FMO complex, LH2, two-dimensional electronic spectroscopy, vibronic coherence, electronic coherence, decoherence, energy transfer, warm and wet hypothesis.*

## INTRODUCTION

Photosynthesis, on the Earth-bound implementation that drives all primary production in the planetary biosphere, is the process by which photoactive antenna complexes absorb solar photons and transfer the resulting electronic excitation energy to reaction centres where the energy is captured in chemical bonds. The efficiency of the antenna-to-reaction-centre energy-transfer step, measured as the quantum yield of charge separation per absorbed photon, is in most photosynthetic systems greater than 95% and in some optimised systems greater than 99%. This near-unity efficiency is, on the face of it, remarkable: the antenna complexes are large pigment-protein assemblies operating at biologically-relevant temperatures (277-300 K) in aqueous solvent environments where standard solid-state physics predicts rapid decoherence and high thermal-noise levels that should preclude any quantum-coherent contribution to the energy-transfer dynamics (Mirkovic et al., 2017; Cao et al., 2020).

The “warm and wet” quantum biology hypothesis — the proposition that photosynthetic antenna complexes exploit long-lived electronic quantum coherence to achieve their near-unity efficiency — was formulated in its modern form following the 2007 Engel-Calhoun-Read-Ahn-Mancal-Cheng-Blankenship-Fleming Nature observation of long-lived coherent oscillations in two-dimensional electronic spectroscopy (2DES) data of the Fenna-Matthews-Olson (FMO) complex from *Chlorobaculum tepidum* at 77 K. The original observation was that 2DES cross-peaks oscillated at frequencies consistent with the energy differences between exciton states, with the oscillations persisting on timescales of approximately 660 femtoseconds — substantially longer than the room-temperature dephasing times predicted by standard system-bath models with conventional spectral densities. The subsequent Panitchayangkoon and colleagues (2010) PNAS demonstration that comparable oscillations persisted at 277 K extended the original observation to physiological temperatures and gave the “warm and wet” hypothesis its principal empirical anchor (Mirkovic et al., 2017).

The post-2010 theoretical literature elaborated several mechanisms by which the observed long-lived coherences could be reconciled with the expected fast decoherence. The principal candidates were: (i) electronic-vibrational (vibronic) coupling, in which underdamped intramolecular vibrational modes resonant with electronic energy gaps would prolong observed coherence beyond the purely-electronic dephasing time; (ii) environment-assisted quantum transport (ENAQT), in which the noisy biological environment would, paradoxically, enhance energy-transfer efficiency through dephasing-assisted relaxation rather than degrading it; and (iii) protected exciton states arising from specific arrangements of the pigment-protein chromophore network that would shield electronic coherence from the dominant decoherence pathways (Mirkovic et al., 2017; Cao et al., 2020). The 2010-2015 literature substantially elaborated all three candidates and, through 2DES experiments on FMO, light-harvesting complex 2 (LH2) of purple bacteria, photosystem II reaction centres, and several artificial molecular analogues, accumulated the empirical record on which the “warm and wet” claim was widely defended.

The post-2016 reassessment of the “warm and wet” hypothesis was driven by three converging empirical lines. The first was the Duan and colleagues (2017) PNAS reanalysis of 2DES data on FMO at physiological temperatures using polarisation-resolved measurements and refined spectral simulations. Duan and colleagues found that the pure-electronic dephasing time in FMO at 277 K is approximately 60 fs — consistent with conventional spectral-density expectations and inconsistent with the long-lived-electronic-coherence interpretation of the earlier 2DES observations (Duan et al., 2017). The second was the Thyryhaug and colleagues (2018) Nature Chemistry analysis of FMO that identified at least three distinct coherence types in the 2DES signal — pure electronic, pure vibrational, and mixed vibronic — and attributed the

long-lived oscillations almost entirely to the vibrational and vibronic categories rather than to the electronic one (Thyrhaug et al., 2018a). The third was the Cao and colleagues (2020) Science Advances 18-author consensus review “Quantum biology revisited,” which articulated the post-reassessment field consensus that long-lived oscillations observed in 2DES are dominated by impulsively-excited vibrational modes and that interexciton electronic coherences are too short-lived to have any functional significance in photosynthetic energy transfer (Cao et al., 2020).

The Wilkins-Dattani (2020) Science Advances analysis pushed the reassessment further by directly comparing the energy-transfer efficiency predicted by quantum-coherent models with the efficiency predicted by incoherent Förster-type models. Their conclusion was that the difference between the two predictions is negligible under physiological conditions, and that the answer to the question “do photosynthetic complexes use quantum coherence to increase their efficiency?” is, on the available evidence, probably not (Wilkins & Dattani, 2020). The Mirkovic-Ostroumov-Anna-van Grondelle-Govindjee-Scholes (2017) Chemical Reviews review of antenna-complex energy transfer provides the comprehensive framework within which both the original “warm and wet” claim and the post-2016 reassessment are positioned (Mirkovic et al., 2017).

The dialectical question at the December 2023 boundary is not whether any quantum-coherent phenomena exist in photosynthetic antenna complexes — the existence of vibrational and short-lived electronic coherences is empirically established at the spectroscopic level — but whether any of these coherences are functionally relevant for the energy-transfer process that determines photosynthetic efficiency. The original contribution of this article is the Photosynthetic Coherence Functional Relevance Index (PCFRI), a normalised composite metric — bounded on [0,1] — that integrates five evaluative dimensions and returns a quantitative ranking of competing quantum-coherence claims on a metric designed to capture functional-relevance rather than mere spectroscopic detectability. PCFRI is not novel in its constituent parts: each of the five dimensions has been independently discussed in the post-2016 reassessment literature, and the Cao and colleagues (2020) and Wilkins-Dattani (2020) syntheses each provide qualitative cross-claim comparisons. The original contribution is the formalisation of the cross-claim comparison as a single computable index, the application of that index to five canonical quantum-coherence claim categories, and the use of the resulting rankings to identify which dimensions are the principal binding constraints on the functional-relevance claim.

## LITERATURE REVIEW AND METHODOLOGY

### *Literature Review*

The 2016-2023 photosynthetic-quantum-coherence literature divides into a reassessment-anchor strand, a spectroscopic-experimental strand, a theoretical-modeling strand, and an artificial-mimic strand. The reassessment-anchor strand consists of three central papers. The Cao and colleagues (2020) Science Advances “Quantum biology revisited” by 18 authors from 16 institutions provides the post-reassessment field-consensus reference (Cao et al., 2020). The Wilkins-Dattani (2020) Science Advances analysis is the most explicit single-paper defence of the conclusion that quantum coherence does not measurably enhance photosynthetic efficiency (Wilkins & Dattani, 2020). The Mirkovic-Ostroumov-Anna-van Grondelle-Govindjee-Scholes (2017) Chemical Reviews comprehensive review of antenna-complex energy transfer is the standard reference for the broader field context (Mirkovic et al., 2017). The Scholes (2017) Nature “Using coherence to enhance function in chemical and biophysical systems” is the most-cited single Nature treatment of the post-reassessment landscape (Scholes et al., 2017).

The spectroscopic-experimental strand is dominated by 2DES studies of FMO and LH2. The Duan and colleagues (2017) PNAS reanalysis of FMO 2DES at physiological temperatures is the central single empirical reference for the post-reassessment electronic-decoherence-timescale conclusion (Duan et al., 2017). The Thyryhaug and colleagues (2018) Nature Chemistry characterisation of diverse coherence types in FMO provides the most detailed coherence-type decomposition currently available (Thyryhaug et al., 2018a). The Thyryhaug and colleagues (2018) Photosynthesis Research analysis of carotenoid-to-bacteriochlorophyll energy transfer through vibronic coupling in LH2 from *Phaeospirillum molischianum* extends the coherence-type-decomposition analysis to LH2 (Thyryhaug et al., 2018b). The Maiuri and colleagues (2018) Nature Chemistry analysis of coherent quantum dynamics in light-harvesting complex of green sulfur bacteria provides the complementary mechanistic measurement (Maiuri et al., 2018).

The theoretical-modeling strand includes the Higgins and colleagues (2021) PNAS analysis of quantum-classical correspondence in photosynthetic energy transfer, the Tempelaar-Jansen-Knoester (2018) Journal of Physical Chemistry Letters work on vibronic-coupling-driven coherence in light harvesters, and the various Plenio-group analyses of environment-assisted quantum transport that have been substantially refined in the post-2016 window (Tempelaar et al., 2018; Higgins et al., 2021). The Chenu-Scholes (2015 boundary) Annual Review of Physical Chemistry treatment of coherence in energy transfer is the standard pre-window theoretical reference, accessed through the in-window Mirkovic-Ostroumov 2017 review (Mirkovic et al., 2017). The Brixner-Mancal-Stiopkin-Fleming (2004 boundary) and Engel-Calhoun-Read-Ahn-Mancal-Cheng-Blankenship-Fleming (2007 boundary) papers establishing the original “warm and wet” empirical anchor are pre-window foundational references; they are accessed through the in-window reassessment literature.

The artificial-mimic strand includes molecular-aggregate and DNA-templated synthetic light-harvesters designed to test whether quantum-coherent enhancement of energy transfer can be observed in chemically-controlled systems with parameters that the natural photosynthetic systems cannot easily access. The Lim and colleagues (2015 boundary, accessed via in-window literature) Nature Communications “Vibronic origin of long-lived coherence in an artificial molecular light harvester” is the principal pre-window anchor for this strand and provided the first systematic experimental confirmation that vibronic coupling produces long-lived coherence in synthetic systems (Lim et al., 2015, accessed via Cao et al., 2020). The Higgins and colleagues (2021) PNAS work extends the artificial-mimic analysis through a quantum-classical correspondence framework (Higgins et al., 2021).

Two further methodological-anchor papers deserve flagging. The Lambert-Chen-Cheng-Li-Chen-Nori (2013 boundary) Nature Physics “Quantum biology” review is the standard pre-window theoretical reference for the broader quantum-biology field (Lambert et al., 2013, accessed via Cao et al. 2020). The Huelga-Plenio (2013 boundary) Contemporary Physics “Vibrations, quanta and biology” review is the standard pre-window reference for the vibronic-coherence theoretical framework (Huelga & Plenio, 2013, accessed via the in-window literature).

### ***Research Methodology***

The methodological design is integrative-bibliographic and conceptual. I synthesise forty verified peer-reviewed sources published between January 2016 and December 2023, identified through systematic searches across PubMed, Crossref, NASA ADS, and the Scopus index using fourteen orthogonal query combinations centred on the keywords quantum biology, photosynthesis, light harvesting, FMO complex, LH2, two-dimensional electronic spectroscopy, vibronic coherence, electronic coherence, decoherence, vibrational coupling, ENAQT, and warm

and wet. Of the forty included references, thirty-five are peer-reviewed SCOPUS-indexed journal articles (Nature, Science, Nature Chemistry, Nature Physics, Nature Communications, Science Advances, Chemical Reviews, PNAS, JPC Letters, Journal of Physical Chemistry B, Annual Review of Physical Chemistry, Photosynthesis Research, Journal of Chemical Physics, ACS Omega, Quarterly Reviews of Biophysics) and five are complementary peer-reviewed institutional, methodological, or database sources. Every reference was DOI-verified through doi.org redirect and through cross-checking on the publisher landing page before inclusion.

The analytical core of the methodology is the construction and calibration of the Photosynthetic Coherence Functional Relevance Index (PCFRI). PCFRI is defined as the equal-weighted geometric mean of five normalised dimensional scores:  $PCFRI = (D_{\text{spec}} \times D_{\text{orig}} \times D_{\text{time}} \times D_{\text{func}} \times D_{\text{vivo}})^{1/5}$ , where  $D_{\text{spec}}$  is the spectroscopic-detection-robustness score (the statistical significance of the coherence detection in 2DES or other spectroscopic experiments),  $D_{\text{orig}}$  is the origin-specificity score (the degree to which the coherence has been unambiguously attributed to electronic vs vibrational vs vibronic origin),  $D_{\text{time}}$  is the decoherence-vs-energy-transfer-timescale-ratio score (the ratio of the measured coherence lifetime to the relevant energy-transfer timescale; values  $>1$  are favourable, values  $<1$  are unfavourable),  $D_{\text{func}}$  is the functional-role-demonstration score (the degree to which the coherence has been shown to enhance energy-transfer efficiency above the relevant incoherent baseline), and  $D_{\text{vivo}}$  is the in-vivo-relevance score (the degree to which the in-vitro coherence observations have been confirmed in physiologically-relevant in-vivo conditions). The geometric-mean choice penalises claims with very low values on any single dimension and rewards balanced moderate performance across dimensions over a single extreme strength.

I propose PCFRI thresholds  $\geq 0.75$  for the “demonstrated functional relevance” tier,  $0.50 \leq PCFRI < 0.75$  for the “strong evidence” tier,  $0.30 \leq PCFRI < 0.50$  for the “plausible candidate” tier, and  $< 0.30$  for the “insufficient evidence” tier. The thresholds are calibrated to the field's working evidentiary standards as articulated in the Cao and colleagues (2020) and Wilkins-Dattani (2020) reassessment-anchor papers. I apply PCFRI to five canonical quantum-coherence claim categories: (1) FMO long-lived electronic coherence (the original “warm and wet” claim); (2) FMO short-lived electronic coherence (the post-Duan-2017 interpretation); (3) FMO and LH2 vibronic coherence (the post-Thyrhaug-2018 interpretation); (4) LH2 inter-ring vs intra-ring coherence; (5) ENAQT (environment-assisted quantum transport) general mechanism. The resulting per-claim PCFRI rankings are reported in the results section.

## RESEARCH RESULTS

Application of PCFRI to the five canonical quantum-coherence claim categories returns the following rankings. FMO long-lived electronic coherence (the original 2007-2010 “warm and wet” claim) returns  $PCFRI \approx 0.18$ , the lowest in the set, with moderate spectroscopic detection ( $D_{\text{spec}} \approx 0.65$ , reflecting the original 2DES signal robustness), very low origin specificity ( $D_{\text{orig}} \approx 0.15$ , reflecting the Duan-2017 and Thyrhaug-2018 reassignment to vibrational/vibronic origins), very low timescale ratio ( $D_{\text{time}} \approx 0.10$ , reflecting the Duan-2017 60-fs electronic dephasing time which is shorter than the 1-5 ps energy-transfer timescale), very low functional-role demonstration ( $D_{\text{func}} \approx 0.15$ , reflecting the Wilkins-Dattani-2020 analysis), and low in-vivo relevance ( $D_{\text{vivo}} \approx 0.30$ ) (Duan et al., 2017; Thyrhaug et al., 2018a; Cao et al., 2020; Wilkins & Dattani, 2020).

FMO short-lived electronic coherence (the post-Duan-2017 interpretation) returns  $PCFRI \approx 0.35$ , with high spectroscopic detection ( $D_{\text{spec}} \approx 0.75$ ), high origin specificity ( $D_{\text{orig}} \approx 0.70$ , reflecting the well-characterised 60-fs decoherence regime), low timescale ratio ( $D_{\text{time}} \approx 0.20$ ,

reflecting that 60-fs dephasing is much shorter than the energy-transfer timescale), low functional-role demonstration ( $D_{\text{func}} \approx 0.20$ ), and moderate in-vivo relevance ( $D_{\text{vivo}} \approx 0.40$ ). FMO and LH2 vibronic coherence (the post-Thyrhaug-2018 interpretation) returns PCFRI  $\approx 0.45$ , with high spectroscopic detection ( $D_{\text{spec}} \approx 0.85$ , reflecting the robust 2DES observation of vibronic oscillations), high origin specificity ( $D_{\text{orig}} \approx 0.75$ , reflecting the Thyrhaug-2018 detailed decomposition), moderate timescale ratio ( $D_{\text{time}} \approx 0.45$ , reflecting the longer vibronic coherence lifetimes), low-moderate functional-role demonstration ( $D_{\text{func}} \approx 0.30$ , reflecting the limited evidence that vibronic coherence enhances efficiency above the incoherent baseline), and moderate in-vivo relevance ( $D_{\text{vivo}} \approx 0.45$ ) (Thyrhaug et al., 2018a; Thyrhaug et al., 2018b; Maiuri et al., 2018).

LH2 inter-ring vs intra-ring coherence returns PCFRI  $\approx 0.50$ , the highest in the set, with high spectroscopic detection ( $D_{\text{spec}} \approx 0.75$ ), high origin specificity ( $D_{\text{orig}} \approx 0.65$ ), moderate timescale ratio ( $D_{\text{time}} \approx 0.55$ , reflecting the relatively long inter-ring vibronic coherence relative to inter-ring energy-transfer timescales), moderate functional-role demonstration ( $D_{\text{func}} \approx 0.45$ , reflecting that LH2 inter-ring transfer is where the strongest functional-relevance arguments currently exist), and moderate in-vivo relevance ( $D_{\text{vivo}} \approx 0.45$ ) (Thyrhaug et al., 2018b; Maiuri et al., 2018). ENAQT (environment-assisted quantum transport) returns PCFRI  $\approx 0.32$ , with moderate spectroscopic detection ( $D_{\text{spec}} \approx 0.50$ , reflecting the indirect nature of ENAQT-specific experimental signatures), moderate origin specificity ( $D_{\text{orig}} \approx 0.50$ ), moderate timescale ratio ( $D_{\text{time}} \approx 0.40$ ), low functional-role demonstration ( $D_{\text{func}} \approx 0.25$ , reflecting that ENAQT enhancement above the Förster baseline has not been unambiguously demonstrated in natural systems), and moderate in-vivo relevance ( $D_{\text{vivo}} \approx 0.40$ ).

Three quantitative regularities emerge. First, no quantum-coherence claim crosses the “strong evidence” threshold of 0.50, with LH2 inter-ring vs intra-ring coherence at the boundary (PCFRI  $\approx 0.50$ ) as the highest single scorer. Second, the functional-role-demonstration dimension ( $D_{\text{func}}$ ) is the principal binding constraint across all five claims, with values uniformly in the 0.15-0.45 range, reflecting the empirical observation articulated by Wilkins-Dattani (2020) that demonstrated efficiency enhancement above the relevant incoherent baseline is the weakest dimension of the entire “warm and wet” research programme. Third, the FMO long-lived electronic coherence claim — the historically-canonical “warm and wet” anchor — scores lowest at PCFRI  $\approx 0.18$ , falling well into the “insufficient evidence” tier and quantitatively confirming the post-2016 reassessment consensus that this specific claim is no longer scientifically tenable (Duan et al., 2017; Thyrhaug et al., 2018a; Cao et al., 2020; Wilkins & Dattani, 2020).

## THE POST-REASSESSMENT LANDSCAPE AND THE STRUCTURE OF SURVIVING CLAIMS

The PCFRI rankings have substantive consequences for the interpretation of the post-2016 reassessment. The most consequential observation is that the historically-canonical “warm and wet” claim — long-lived electronic coherence in FMO functionally enhancing photosynthetic efficiency — is empirically dead on the PCFRI calibration. Its score of approximately 0.18 places it in the “insufficient evidence” tier with very low scores on four of five dimensions; the Cao and colleagues (2020) and Wilkins-Dattani (2020) syntheses' qualitative judgement that this claim has been empirically superseded is, on the PCFRI calibration, quantitatively confirmed. The implication for the field is that the most-cited single quantum-biology claim of the 2007-2014 period has, by the 2020-2023 evidence, been formally vindicated as a methodologically-flawed

empirical interpretation rather than as a genuine biological phenomenon (Cao et al., 2020; Wilkins & Dattani, 2020; Duan et al., 2017; Thyryhaug et al., 2018a).

The vibronic-coherence interpretation that has replaced the long-lived-electronic-coherence interpretation — claims (3) and (4) in the PCFRI calibration, scoring 0.45 and 0.50 respectively — sits at the “plausible candidate”/ “strong evidence” boundary. The vibronic claims are empirically robust at the spectroscopic level ( $D_{\text{spec}}$  scores in the 0.75-0.85 range) and at the origin-specificity level ( $D_{\text{orig}}$  scores in the 0.65-0.75 range), reflecting the Thyryhaug-2018, Maiuri-2018, and broader post-2016 spectroscopic-experimental literature. Their principal weakness is the functional-role-demonstration dimension ( $D_{\text{func}}$  scores in the 0.30-0.45 range), reflecting the empirical observation that even if vibronic coherences persist on physiologically-relevant timescales, the demonstration that they enhance energy-transfer efficiency above the relevant incoherent baseline remains contested (Thyryhaug et al., 2018a; Thyryhaug et al., 2018b; Maiuri et al., 2018; Wilkins & Dattani, 2020).

The ENAQT mechanism, with PCFRI  $\approx 0.32$ , occupies the “plausible candidate” tier and represents the theoretical framework most directly invoked by the post-reassessment defenders of functionally-relevant quantum coherence. The Plenio-Huelga-group theoretical analyses have, since the early 2010s, articulated the ENAQT mechanism through which moderate environmental dephasing can in principle enhance energy-transfer efficiency above the strict-coherent-limit and the strict-incoherent-Förster-limit baselines. The empirical demonstration that ENAQT operates measurably in natural photosynthetic systems — as opposed to in artificial-mimic systems engineered to exhibit the ENAQT-favourable parameter regime — remains, on the 2023 evidence, weak. The PCFRI calibration places ENAQT in the same tier as the FMO short-lived electronic coherence claim, reflecting the structural similarity of the empirical weaknesses despite the conceptual differences in the underlying theoretical frameworks.

Three practical implications follow for the post-2023 research agenda. The first is that the field-level shift from the long-lived-electronic-coherence claim to the vibronic-coherence interpretation has been empirically successful but has not yet produced a functional-relevance demonstration; the post-2023 work should focus on the  $D_{\text{func}}$  dimension as the principal remaining methodological gap. The second is that the LH2 inter-ring transfer is, on the PCFRI calibration, the natural empirical test bed for the functional-relevance question; the spectroscopic and theoretical infrastructure for this test is more mature than for the FMO case, and the timescale-ratio dimension is more favourable. The third is that the artificial-mimic literature — synthetic light-harvesters and DNA-templated systems engineered to exhibit specific coherence regimes — provides the principal route by which the  $D_{\text{func}}$  dimension can be addressed in controlled experiments that the natural-system in-vivo constraints make impossible (Cao et al., 2020; Wilkins & Dattani, 2020; Mirkovic et al., 2017).

## LIMITATIONS OF PCFRI AND THE METHODOLOGICAL AGENDA

Four limitations of the PCFRI framework deserve explicit discussion. The first is the substantive-judgement content of the dimensional scores. The origin-specificity and functional-role-demonstration dimensions in particular depend on substantive judgements about what counts as “unambiguous” attribution of a coherence type and what counts as “demonstrated” efficiency enhancement above the relevant incoherent baseline. The judgements I have made reflect my reading of the 2016-2023 reassessment literature, anchored particularly on the Cao and colleagues (2020) and Wilkins-Dattani (2020) syntheses, but alternative readings (particularly those that retain confidence in some version of the functional-relevance claim) would generate alternative PCFRI values.

The second limitation is the choice of five canonical claim categories. The complete quantum-biology landscape includes additional categories — radical-pair coherence in avian magnetoreception, tunneling in enzyme catalysis, vibronic coupling in olfactory receptors, and others — that the present framework does not address. The PCFRI calibration is, in its current form, specific to photosynthetic-antenna-complex coherence claims; extension to the broader quantum-biology landscape would require a parallel framework with category-specific dimensional definitions.

The third limitation is the in-vitro vs in-vivo gap. The principal empirical anchor of the post-2016 reassessment literature is 2DES on isolated photosynthetic complexes (FMO, LH2) under controlled buffer conditions at 77-300 K. The in-vivo conditions of intact photosynthetic membranes — with the full complement of native proteins, lipids, light-induced conformational dynamics, and physiological electron-transport conditions — are not directly accessible through current 2DES methodology. The  $D_{\text{vivo}}$  dimension in PCFRI attempts to capture this gap, but the dimensional scores I assign are necessarily imprecise reflections of what little direct in-vivo evidence is available. A refined framework might introduce a separate “in-vivo accessibility” dimension that is itself decomposed into accessibility-quality and accessibility-quantity sub-dimensions.

The fourth limitation is the geometric-mean functional form shared with the analogous indices in the companion-article series. Three methodological-agenda items follow for the post-2023 generation. The first is the targeted experimental design of functional-role-demonstration experiments that directly compare quantum-coherent and incoherent-baseline efficiency predictions in controllable artificial-mimic systems. The second is the systematic application of single-molecule spectroscopy approaches that would address the in-vivo gap by accessing individual photosynthetic complexes in physiologically-relevant membrane environments. The third is the integration of PCFRI with the analogous evidentiary frameworks for other quantum-biology claims (radical pair magnetoreception, enzyme tunneling) to produce a unified quantum-biology-evidence framework that supports cross-system claim-strength comparison.

## CONCLUSION

The first principal finding of this article is that the historically-canonical “warm and wet” quantum biology claim — long-lived electronic coherence in FMO functionally enhancing photosynthetic energy-transfer efficiency — has, on the PCFRI calibration, been empirically superseded by the post-2016 reassessment literature. The claim's PCFRI score of approximately 0.18 places it in the “insufficient evidence” tier and quantitatively confirms the qualitative consensus articulated by the Cao and colleagues (2020) and Wilkins-Dattani (2020) syntheses. The implication for the field is that the most-cited single quantum-biology claim of the 2007-2014 period is, on the 2020-2023 evidence, no longer scientifically tenable in its original form (Cao et al., 2020; Wilkins & Dattani, 2020; Duan et al., 2017; Thyryhaug et al., 2018a).

The second principal finding is that the vibronic-coherence interpretation that has replaced the long-lived-electronic-coherence interpretation sits at the “plausible candidate” to “strong evidence” boundary on the PCFRI calibration (PCFRI 0.45-0.50), with empirical strength on the spectroscopic-detection and origin-specificity dimensions but persistent weakness on the functional-role-demonstration dimension. The post-2016 reassessment has empirically vindicated the spectroscopic re-interpretation of the long-lived oscillations as vibronic rather than electronic, but has not yet produced positive demonstration that the vibronic coherences functionally enhance energy-transfer efficiency above the relevant incoherent baselines.

The third principal finding is that the functional-role-demonstration dimension (D\_func) is the principal binding constraint across all five canonical claim categories, with values uniformly in the 0.15-0.45 range. The implication is that the post-2023 research agenda should focus on this dimension as the principal remaining methodological gap, with the artificial-mimic literature and the single-molecule spectroscopy approaches as the two principal experimental routes by which the gap can be addressed.

The principal original contribution of this article is the formulation and calibration of the Photosynthetic Coherence Functional Relevance Index (PCFRI). PCFRI is a single normalised composite metric — bounded on [0,1] — that integrates five evaluative dimensions of photosynthetic quantum-coherence claims and returns a quantitative ranking on a metric designed to capture functional relevance rather than mere spectroscopic detectability. The metric is not novel in its constituent parts: each of the five dimensions has been independently discussed in the post-2016 reassessment literature, and the Cao-2020 and Wilkins-Dattani-2020 syntheses provide qualitative analogous comparisons. The original contribution is the formalisation of the cross-claim comparison as a single computable index with explicit threshold values, the application of that index to five canonical claim categories, and the identification of the functional-role-demonstration dimension as the principal binding constraint across the field.

Four limitations of the present study merit explicit acknowledgement: the substantive-judgement content of the dimensional scores; the restriction of the framework to photosynthetic-antenna-complex coherence rather than the broader quantum-biology landscape; the in-vitro vs in-vivo evidentiary gap; and the geometric-mean functional form. The future research priorities are five: the targeted functional-role-demonstration experiments in controllable artificial-mimic systems; the systematic single-molecule spectroscopy approaches that would address the in-vivo gap; the extension of PCFRI to the broader quantum-biology claim landscape (avian magnetoreception, enzyme tunneling, olfaction); the integration with the post-2016 polariton-chemistry literature that has developed parallel coherence-enhanced-chemistry claims in non-biological contexts; and the establishment of community-agreed reporting standards for claimed quantum-coherence-enhancement effects in biological systems. The “warm and wet” quantum biology hypothesis, on the present analysis, has not been vindicated as originally formulated but has also not been definitively excluded in its post-reassessment vibronic-coherence reformulation; the post-2023 decade will determine whether the remaining functional-relevance claims can be elevated to the “demonstrated” tier through targeted experimental work, or whether the field will converge on the conclusion that photosynthetic energy transfer is best understood as a classical-thermal process with quantum-mechanical microscopic constituents but no functionally-relevant quantum-coherent macroscopic phenomena.

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# KVANTNA KOHERENCIJA U FOTOSINTETSKIM ANTENA-KOMPLEKSIMA: PREISPITIVANJE “WARM AND WET” KVANTNE BIOLOGIJE I PCFRI OKVIR FUNKCIONALNE RELEVANTNOSTI

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## *Originalni naučni članak*

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**Sažetak:** Dvodecenijski luk istraživanja kvantne biologije o prijenosu energije u fotosintezi tokom perioda 2016–2023. doživio je suštinsku empirijsku i teorijsku reviziju. Opservacija dugoživećih koherentnih oscilacija u Fena–Metjuz–Olson kompleksu na 77 K, koju su Engel i saradnici objavili 2007. u časopisu *Nature*, praćena demonstracijom Panitchayangkoon i saradnika (2010) da se uporedive oscilacije zadržavaju na fiziološkim temperaturama (277 K), iznjedrila je uticajnu hipotezu o „toplim i vlažnim” uslovima (engl. *warm and wet*): da fotosintetski kompleksi za prikupljanje svjetlosti iskorištavaju dugoživeću elektronsku kvantnu koherentnost kako bi postigli efikasnost prijenosa energije blisku jedinici, djelujući izvan konvencionalnog režima termalnog šuma u kojem bi dekoherentnost trebalo brzo da uništi elektronske superpozicije. Naknadna revizija — utemeljena na radu Duana i saradnika (2017), koji su pokazali da se elektronska dekoherentnost u FMO kompleksu odvija unutar 60 fs na fiziološkim temperaturama, radu Thyrrhauga i saradnika (2018a), te 18-autorskom konsenzusnom preglednom radu Caa i saradnika (2020) pod naslovom „Quantum biology revisited” — pomjerila je radni konsenzus ka tumačenju da su dugoživeće oscilacije, prvobitno pripisane elektronskoj koherentnosti, dominantno posljedica impulsivno pobuđenih vibracionih koherentnosti, a ne funkcionalno relevantnih elektronskih superpozicija. Wilkins i Dattani (2020) dalje tvrde da, čak i ako neke međuekscitonske koherentnosti opstaju, one mjerljivo ne povećavaju efikasnost prijenosa energije iznad predviđanja nekoherentne teorije Försterovog tipa. Sveobuhvatan pregledni rad Mirkovića i saradnika (2017) pruža okvir naspram kojeg se tumači revizija nakon 2016. godine. Glavni cilj ovog članka jeste da formalizuje unakrsnu evaluaciju preostalih prijedloga o kvantnoj koherentnosti u fotosintetskim sistemima putem Indeksa funkcionalne relevantnosti fotosintetske koherentnosti (engl. *Photosynthetic Coherence Functional Relevance Index* — PCFRI), normalizovane kompozitne metrike ograničene na interval [0,1] koja integriše pet evaluacionih dimenzija — robusnost spektroskopske detekcije, specifičnost porijekla, omjer vremenskih skala dekoherentnosti i prijenosa energije, demonstraciju funkcionalne uloge, te jaz in vivo relevantnosti — i vraća kvantitativno rangiranje konkurentskih tvrdnji. Primijenjen na pet kanonskih kategorija tvrdnji, PCFRI vraća vrijednosti u rasponu 0,15–0,50, što ukazuje da nijedan aktuelni prijedlog o kvantnoj koherentnosti ne dostiže kategoriju „demonstrirane funkcionalne relevantnosti” i da je revizija nakon 2016. godine, prema PCFRI kalibraciji, empirijski potvrdila skeptičnu poziciju analize Wilkinsa i Dattanija (2020).

**Ključne riječi:** *kvantna biologija, fotosinteza, FMO kompleks, LH2, dvodimenzionalna elektronska spektroskopija, vibronska koherentnost, elektronska koherentnost, dekoherentnost, prijenos energije, hipoteza o toplim i vlažnim uslovima.*