

# Quantum Coherence in Photosystem II: Environment-Assisted Transport and the Role of Vibronic Coupling in Biological Light-Harvesting

## Quantum Coherence in Photosystem II: Environment-Assisted Transport and the Role of Vibronic Coupling in Biological Light-Harvesting

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### Abstract

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The discovery of long-lived quantum coherence in photosynthetic light-harvesting complexes—first reported in the Fenna-Matthews-Olson (FMO) complex in 2007—fundamentally challenged the assumption that biological systems operate exclusively in the classical regime at physiological temperatures. Over the subsequent two decades, experimental and theoretical work has revealed a nuanced picture: quantum coherence persists on femtosecond-to-picosecond timescales and contributes to the remarkable near-unity quantum efficiency of photosynthetic energy transfer. We review the current state of evidence across multiple photosynthetic systems, with emphasis on Photosystem II (PSII), and synthesize recent theoretical developments including environment-assisted quantum transport (ENAQT), vibronic enhancement, and the role of non-Markovian spectral densities. We identify three open questions: (1) whether coherence is functional or epiphenomenal, (2) how the protein scaffold actively tunes spectral densities to optimize transport, and (3) what design principles from biological light-harvesting can inform artificial quantum technologies. We propose that PSII's oxygen-evolving complex provides a uniquely constrained testbed for resolving these questions.

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### 1. Introduction

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Photosynthesis converts approximately 130 TW of solar energy into chemical free energy annually, making it the dominant energy conversion process on Earth [established]. The initial step—light absorption followed by excitation energy transfer (EET) to a reaction center—operates with quantum efficiencies approaching unity under low-light conditions. Understanding how this efficiency is achieved has implications for both fundamental biophysics and the design of artificial light-harvesting devices.

The canonical picture of EET, established by Förster in the 1940s, treats excitation transfer as incoherent hopping between weakly coupled chromophores mediated by dipole-dipole coupling [established]. This framework successfully describes energy transfer over distances exceeding  $\sim 2$  nm, where electronic couplings are small compared to thermal energy ( $k_B T \approx 200 \text{ cm}^{-1}$  at room temperature). However, in densely packed antenna complexes where chromophore separations are  $\sim 1$  nm or less, electronic couplings can approach  $100 - 500 \text{ cm}^{-1}$ , and the Förster picture breaks down.

The landmark 2007 experiment by Engel et al. [1] demonstrated quantum beating in the FMO complex of green sulfur bacteria at 77 K, with subsequent work extending the observation to physiological temperatures [2]. These results initiated an intense research program investigating whether quantum coherence plays a functional role in photosynthetic efficiency or is merely a spectroscopic artifact observable only under artificial conditions.

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## 2. Spectroscopic Evidence

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### 2.1 The FMO Complex

The FMO complex of green sulfur bacteria (*Chlorobaculum tepidum*) has served as the primary model system for quantum coherence studies due to its structural simplicity (a homotrimer of seven bacteriochlorophyll-*a* molecules per monomer) and water solubility. Two-dimensional electronic spectroscopy (2DES) experiments have consistently revealed oscillatory signals in the cross-peak amplitude lasting 300 — 660 fs at physiological temperatures [1,2,3].

The interpretation of these oscillations, however, has undergone significant revision. Early analyses attributed the beating to purely electronic coherences between excitonic states. Subsequent work demonstrated that vibrational coherences—particularly from underdamped intramolecular modes in the 200 — 500  $\text{cm}^{-1}$  range—can produce similar spectroscopic signatures [4]. The current consensus, summarized by Cao et al. (2020) [5], is that both electronic and vibrational coherences contribute, with vibronic (mixed electronic-vibrational) coherence being the dominant observable at room temperature.

### 2.2 Light-Harvesting Complex II (LHCII)

LHCII, the major antenna complex of plants, presents a more challenging target due to its larger size and spectral congestion. Nevertheless, 2DES experiments by Schlau-Cohen et al. [6] and subsequent work have identified coherence lifetimes of  $\sim 200$  fs at 293 K, shorter than FMO but still exceeding the timescale of individual energy transfer steps.

### 2.3 Photosystem II Core Complex

Direct spectroscopic evidence for quantum coherence within the PSII core complex remains limited compared to FMO and LHCII. The PSII core contains approximately 35 chlorophyll-*a* molecules, 2 pheophytins, and the oxygen-evolving complex (OEC)—a  $\text{Mn}_4\text{CaO}_5$  cluster that catalyzes water oxidation. The spectral density of chlorophyll-*a* in the  $Q_y$  band (650-700 nm) creates significant overlap, making it difficult to isolate individual pigment contributions in 2DES experiments.

Recent advances in structure-based modeling, leveraging the 1.9 Å resolution crystal structure of PSII [7], have begun to address this gap. Novoderezhkin et al. [8] employed modified Redfield theory to model exciton dynamics in the full PSII core, predicting coherence lifetimes of 100-200 fs at room temperature, with coherent contributions to the overall transfer efficiency estimated at 10 — 20%.

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## 3. Theoretical Frameworks

### 3.1 Environment-Assisted Quantum Transport (ENAQT)

The ENAQT paradigm, formalized by Mohseni, Rebentrost, Lloyd, and Aspuru-Guzik (2008) [9], proposes that environmental noise can enhance, rather than degrade, quantum transport efficiency in systems with static disorder. The central insight is that in a purely coherent system, Anderson localization due to energetic disorder can trap excitations, preventing them from reaching the reaction center. Moderate dephasing noise breaks localization without fully destroying coherence, enabling diffusive transport toward the target.

The ENAQT model produces a characteristic non-monotonic relationship between dephasing rate and transport efficiency that peaks at an optimal noise level  $\gamma_{\text{opt}}$ . Experimental evidence for ENAQT in photosynthetic systems remains indirect but suggestive: the FMO complex's energy transfer efficiency is robust against mutations that alter

pigment site energies [10], consistent with a mechanism that does not require fine-tuning of electronic Hamiltonian parameters.

### 3.2 Vibronic Coupling and Non-Markovian Dynamics

A key limitation of early ENAQT models was the assumption of Markovian (memoryless) system-bath interactions. Photosynthetic environments exhibit structured spectral densities with distinct peaks corresponding to protein vibrational modes. These modes introduce memory effects that require non-Markovian treatments.

The Hierarchical Equations of Motion (HEOM) approach [11,12] provides a numerically exact framework for non-Markovian dynamics in systems with arbitrary spectral densities. HEOM simulations have demonstrated that underdamped vibrational modes ( $\omega \sim 200 - 500 \text{ cm}^{-1}$ ) can enhance coherence lifetimes, and that vibronic mixing between electronic excitations and specific vibrational modes can create transport channels that bypass energetic bottlenecks [speculative].

### 3.3 Modified Redfield and Förster Theory

For intermediate coupling regimes—between the fully coherent (excitonic) and fully incoherent (Förster) limits—generalized Förster and modified Redfield theories provide computationally tractable alternatives to HEOM. The modified Redfield approach has been extensively applied to PSII core complex modeling [8], yielding predictions that agree qualitatively with HEOM.

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## 4. Photosystem II as a Model System

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### 4.1 Structural Organization

The PSII core complex is organized around two branches of cofactors (D1 and D2) embedded in a heterodimeric protein scaffold. The arrangement creates an energetic funnel: peripheral antenna chlorophylls absorb at shorter wavelengths ( $\sim 670 \text{ nm}$ ), with excitation energy cascading toward the reaction center chlorophylls  $P_{D1}$  and  $P_{D2}$  ( $\sim 680 \text{ nm}$ ) where charge separation occurs.

### 4.2 The Oxygen-Evolving Complex Constraint

PSII's defining feature—the OEC—imposes a unique functional constraint: the four-electron oxidation of water ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$ ) requires precise timing of sequential charge separations. The Kok cycle (S-states  $S_0$  through  $S_4$ ) must advance reliably despite fluctuating illumination, imposing evolutionary pressure on the upstream energy transfer network to maintain robust delivery under variable conditions [speculative].

This constraint suggests a possible functional role for quantum coherence in PSII: transient delocalization of excitation energy across multiple pigments could smooth out fluctuations in light intensity, ensuring consistent advancement through the S-state cycle [my conjecture]. Direct experimental testing of this hypothesis remains an open challenge.

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## 5. Open Questions

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### Q1: Is quantum coherence functional or epiphenomenal?

*Current status:* [debated]. Evidence from mutation studies in FMO [10] and LHCII [13] suggests that coherence lifetimes can be altered without significantly degrading overall efficiency, consistent with an epiphenomenal interpretation. However, these studies were conducted under steady-state illumination; the functional role of coherence may manifest only under fluctuating light conditions.

*Proposed experiment:* Measure PSII oxygen evolution as a function of illumination flicker frequency (1 Hz to 1 kHz), comparing wild-type with mutants that alter chromophore site energies. If coherence provides robustness against fluctuations, efficiency should degrade more steeply in mutants as flicker frequency increases.

*Falsifiability:* This would be disconfirmed if oxygen evolution efficiency shows no differential sensitivity to flicker frequency between wild-type and site-energy mutants.

### Q2: How does the protein scaffold tune spectral densities?

*Current status:* [speculative]. While the general principle—that protein vibrational modes couple to electronic excitations—is well-established [established], the specific protein structural features that determine spectral density peaks remain poorly characterized.

### Q3: Can biological design principles inform artificial quantum technologies?

*Current status:* [speculative]. The ENAQT concept has been demonstrated in engineered systems including superconducting qubit arrays [14] and biomimetic porphyrin arrays [15]. Translation to practical device design remains nascent.

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## 6. Design Principles for Artificial Light-Harvesting

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The biological solution to efficient energy transfer under noisy, fluctuating conditions offers several design principles:

1. **Moderate coupling regime:** Operating at the ENAQT sweet spot where dephasing enhances rather than degrades transport.
  2. **Vibronic enhancement:** Exploiting specific vibrational modes of the scaffold to create resonant transport channels.
  3. **Energetic funneling:** A downhill free energy landscape that biases transport toward the target.
  4. **Redundancy:** Multiple parallel transport pathways that provide robustness against localized damage.
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