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Quantitative modeling of energy dissipation in *Arabidopsis thaliana*

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ABSTRACT

In photosynthesis, solar energy is absorbed and converted into chemical energy. Chlorophyll embedded in proteins absorb light and transfer excitation energy to reaction centers where charge separation occurs. However, the solar flux incident on photosynthetic organisms is highly variable, requiring complex feedback systems to regulate the excitation pressure on reaction centers and prevent excess absorbed energy from causing damage. During periods of transient high light, excess absorbed energy is dissipated as heat. This is routinely observed as the quenching of chlorophyll fluorescence, and often broadly referred to as non-photochemical quenching (NPQ). Understanding the mechanisms through which photosynthetic systems dissipate excess energy and regulate excitation pressure in response to variable light conditions requires extensive quantitative modeling of the photosynthetic system and energy dissipation to interpret experimental observations. This review discusses efforts to model energy dissipation, or quenching, in *Arabidopsis thaliana* and their connections to models of regulatory systems that control quenching. We begin with a review of theory used to describe energy transfer and experimental data obtained to construct energy transfer models of the photosynthetic antenna system that underlie the interpretation of chlorophyll fluorescence quenching. Second, experimental evidence leading to proposed molecular mechanisms of quenching and the implications for modeling are discussed. The initial incorporation of depictions of proposed mechanisms into quantitative energy transfer models is reviewed. Finally, the necessity of connecting energy transfer models that include molecular models of quenching mechanisms with regulatory models is discussed.

1. Introduction

Photosynthesis is the process by which organisms absorb sunlight to drive electron transfer and energy storage, but excess sunlight can damage the organism (Blankenship, 2014). The natural fluctuations in light intensity experienced by plants require processes that dissipate energy absorbed in excess of what can be used productively, and that can be rapidly optimized to the light condition (Külheim et al., 2002). Of the two photosystems in higher plants, photoprotection in photosystem II (PSII) has been extensively studied. The suite of dissipative, or photoprotective, mechanisms that protect PSII collectively result in, and are referred to as, non-photochemical quenching (NPQ): the reduction in chlorophyll *a* fluorescence yield due to dissipation of excess excitation by mechanisms other than photochemistry (Demmig-Adams and Adams, 1992; Niyogi, 1999; Ruban, 2016).

NPQ is a broad term encompassing several constituent components often separated into q_E, the rapidly reversible, energy-dependent (pH-dependent) quenching component, and q_I, the slowly reversible component associated with PSII photoinhibition (Krause and Weis, 1991; van Kooten and Snel, 1990; Wraight and Crofts, 1970). Although important in many photosynthetic systems, q_T, a component of NPQ associated with excitation balance between PSI and PSII by altering the relative antenna size, does not contribute significantly in vascular plants, such as *Arabidopsis thaliana*, exposed to high light (Niyogi, 1999). q_E and another related NPQ component termed q_Z (Nilkens et al., 2010) have been the subject of intense study. While there is little consensus surrounding the numerous proposed molecular mechanisms (Duffy and Ruban, 2015) underlying the quenching pathways intrinsic to NPQ in PSII, many elements of the regulation of photoprotection are widely agreed upon (Demmig-Adams et al., 2014). Modeling (Laisk et al., 2009) the proposed mechanisms in the context of the photosynthetic energy transfer network and in the context of the regulatory system provides a powerful way to evaluate whether, and in what way, proposed mechanisms play a role in dissipating energy to protect the photosynthetic solar collection apparatus.

One approach to modeling quenching in the photosynthetic system

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is to construct a model capable of predicting experimental measurements, including, e.g., of the fluorescence lifetimes of the *in vivo* system, from quantum and statistical mechanical first principles, structural and spectroscopic data of individual pigments and pigment protein complexes, and membrane imaging (Amarnath et al., 2016). A model must be capable of appropriate treatment of the absorption of light by antenna (Müh et al., 2010; Müh and Renger, 2012; Renger et al., 2011), the transfer of energy to reaction centers (Bennett et al., 2013), and the charge separation process (Novoderezhkin et al., 2011b) to provide a system in which various mechanisms of quenching can be evaluated. Absorption, energy transfer, and charge separation are fundamentally quantum mechanical in their nature. However, to provide a physically meaningful picture, a model must span length scales from angstroms to hundreds of nanometers. To do so requires multiscale modeling and course graining by making appropriate approximations to simplify much of the quantum dynamical calculations; treating the entire system quantum mechanically is impractical, even for modern supercomputers (Kreisbeck and Aspuru-Guzik, 2016). Fortunately, a number of approximations can be made to allow for a model that contains enough of the quantum mechanical features to adequately represent the system. Even so, an accurate model of the system must still integrate data from numerous areas of photosynthesis, making the building of accurate models challenging.

A second area of study that incorporates modeling is the regulatory function of the plant systems that controls the extent of quenching in the photosynthetic antenna (Zaks et al., 2012). The regulatory system operates on timescales from seconds to the lifespan of the plant, but the timescales of greatest interest for regulating the rapid response include changes in the chemical environment of the thylakoid membrane over timescales of seconds to minutes. Current knowledge indicates that a fundamental trigger for inducing quenching is the formation of a transthylakoid pH gradient that, in turn, activates various proteins that influence the actual quenching (Ruban et al., 2012). One of these is the enzyme violaxanthin de-epoxidase that converts violaxanthin to antheraxanthin and zeaxanthin on a timescale of a few minutes when intrathylakoid pH is low (Jahns et al., 2009). These xanthophylls are important players in the molecular mechanisms of quenching and play a number of roles in the pigment protein complexes that effect the ultrafast dynamics of energy transfer. Chemical regulatory models seek to describe quantitatively how the multiple components contribute to the plant system's regulatory response that controls the quenching.

Important open questions include the importance of various quenching mechanisms identified experimentally, and models of how the biochemical regulatory systems control the activation of potential quenching mechanisms. The dynamic nature of the light incident on plants (Külheim et al., 2002) may imply that various mechanisms could play important roles at different times of day or in different patterns of light variability, suggesting that integrated models of the quenching processes and the regulatory response are key for insight into the potential for optimization (Zhu et al., 2004) of various elements of the quenching mechanisms and regulatory system in order to increase crop yields (Kromdijk et al., 2016) or design biomimetic solar energy devices (Terazono et al., 2011). This review focuses on efforts to model energy dissipation mechanisms using multiscale models that integrate the understanding of structure and function of energy-transfer networks, quenching mechanisms, and chemical regulatory systems that are all necessary for developing the level of understanding and tools required to eventually begin engineering quenching systems.

2. Models of energy transfer for evaluating quenching mechanisms

Upon absorption of a photon by a chlorophyll molecule in the photosynthetic system, the energy absorbed may be transferred to reaction centers where charge separation occurs that drives down-stream chemical reactions. When reaction centers are unable to productively accept the energy absorbed by antenna chlorophyll, the photosynthetic system must dissipate the excess energy to prevent unwanted generation of reactive oxygen species.

Historically, the flow of energy through the system has been described using either "lake" or "puddle" models (Robinson, 1967) that describe transfer within the antenna and to the reaction centers. In a lake model, reaction centers sit embedded in a common pool of antenna; in a puddle model, each reaction center has its own antenna. Intermediate cases were described using a variety of connected unit (Lavorel and Joliot, 1972) and domain models (Den Hollander et al., 1983; Paillotin et al., 1979) to define or model transfer within and between antennas and reaction centers. These types of models still implicitly facilitate the interpretation of many studies of quenching behavior, and provide intuition about the photosynthetic system, but are unsuitable for quantitatively evaluating molecular mechanisms and models of quenching as it is difficult to distinguish between these models with experimental data (Bernhardt and Trissl, 1999).

In order to accurately describe the energy transfer process in a quantitative model, appropriate theories to describe the processes involved as well as information about the parameters of the photosynthetic system are required. The theories and data necessary to develop the parameters have all been areas of intense study, spanning from electronic structure of chlorophyll molecules that serve as the primary molecule used to capture photons in individual pigment-protein complexes to the mesoscopic structure of the photosynthetic membrane. These elements can be integrated into a mathematical description of the energy-transfer network that allows for a quantitative prediction of the behavior of absorbed photons and, in turn, predictions of experimental observables such as the fluorescence lifetimes of a photosynthetic system under varying conditions. The most recent efforts build upon many years of work.

2.1. Models of energy transfer processes

For very simple quantum mechanical systems, such as an isolated atom, all the information necessary to describe the time evolution of the system can be contained in a mathematical operator called the Hamiltonian (Atkins and Friedman, 2011). However, even for systems as simple as a single molecule in solution, much of the information in the Hamiltonian cannot be specified exactly, and therefore describing the time evolution requires a statistical approach. A common approach is to partition the complete description into a system of interest and average over the remaining environment (Mukamel, 1995). To describe energy transfer in pigment-protein complexes of the photosynthetic system, the system of interest commonly includes chlorophyll molecules, or chromophores, where energy in the system is absorbed and can flow towards where charge separation occurs. The environment usually consists of the protein matrix that holds the chromophores and surrounding solvent (van Amerongen et al., 2000).

A fundamental concept used to describe electronic excitations is the exciton, a term describing excitation that may be delocalized, or spread, across more than one molecule due to electronic coupling between the molecules (Scholes and Rumbles, 2006). Although this is applicable to a wide range of semiconductor and molecular systems, excitons in photosynthetic systems delocalize over one or a few chromophores due to differences in the strength of electronic interactions within a chromophore and those between neighboring chromophores. This allows for the construction of a relatively simple quantum mechanical model that treats each chromophore as a "site" where a share of the exciton can be located (Fassioli et al., 2014).

The energy gap between the ground and excited electronic state in a specific sites is referred to as the site energy (Cheng and Fleming, 2009; Hu et al., 2002; Mirkovic et al., 2017; Renger et al., 2001). In an ensemble, similar sites generally exhibit a distribution of energy gaps. When a site is excited, energy is stored in the system. The transfer of excitation between sites can then be described quantitatively using an