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Long-Range Electron Transfer through Proteins and Solvents

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Reactions in which electrons tunnel long distances from donors (D) to acceptors (A) pervade solid-state physics, chemistry and biology. Theory suggests that the barriers to these tunneling processes depend strikingly on the composition and structure of the intervening medium. Poor coupling across nonbonded interfaces produces a strong bias in favor of covalent and hydrogen-bonded pathways between redox sites in proteins. The coupling disparity between bonded and nonbonded interfaces accounts in large part for the finding that protein electron-transfer rates do not exhibit a uniform dependence on distance, but instead depend critically on the composition of the medium between redox sites. Rates at a single D-A separation can differ by three orders of magnitude and D-A distances that differ by as much as 0.5 nm can produce identical rates. Our investigations of electron tunneling through proteins and solvents are aimed at elucidating the factors that determine long-range D-A couplings.