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Quantum mechanical hysteresis and the electron transfer problem

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Abstract

We study a simple quantum mechanical symmetric donor–acceptor model for electron transfer (ET) with coupling to internal deformations. The model contains several basic properties found in biological ET in enzymes and photosynthetic centers; it produces tunnelling with hysteresis thus providing a simple explanation for the slowness of the reversed rate and the near 100% efficiency of ET in many biological systems. The model also provides a conceptual framework for the development of molecular electronics memory elements based on electrostatic architectures.
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The physics of electron transfer (ET) is of paramount importance in many fundamental aspects of molecular biology, from photosynthesis [1], to mitochondrial ET, to many control reactions and signalling through the cell membrane [2–4]. Being a sophisticated quantum mechanical tunnelling process in itself, the ET problem includes many aspects of coupling to vibrational degrees of freedom, tunnelling

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control through external variables, and non-reversibility aspects [2]. After the pioneering work of Marcus [5] in the electrochemical aspects of ET for redox reactions in solution, the problem has seen several times renewed interest in both the semiclassical and quantum mechanical (QM) aspects. This is an area where there is a strong interplay between QM and important biological effects at the molecular level.

In addition, there is considerable evidence now on the importance of nonlinear contributions to many important dynamic aspects of molecular biology. DNA dynamics and denaturation [6,7] and signal transduction and coordination of events during the DNA readout by proteins [8,9] have both been ascribed to nonlinearities. The nonlinear character of the hydrogen bonding potential among DNA bases has been known for a very long time [4,10,11]. But nonlinearities in biology are believed to play also a substantial role in ET and energy transfer. Resonant dipole–dipole interactions of the amide I band combined with structural deformations in alpha-helical proteins have been proposed for a very long time as a possible explanation for energy transport from the hydrolysis of ATP [12]. There is experimental evidence that amide I vibrations are coupled nonlinearly; an example being their unusually long life in simple proteins [13]. The coupling of carriers to conformational degrees of freedom has been suggested also to exist in connection with ET from the active prosthetic groups inside cytochromes [4]. There seems to be, in addition, substantial evidence that a nonlinear coupling is required to explain the so-called *gated ET reactions* between quinones in the photosynthetic reaction centers [14]. Knapp and coworkers [15] were among the first to realize the importance of both nonlinearities and Davidov-like solitons [4] in the ET problem. They argued that the construction of the initial and final wave functions in terms of solitary states leads automatically to localization for a symmetric donor–acceptor system, a very desirable model property in many cases, as we shall explain later.

The brief outline given above highlights the fact that there is a case in many real biological systems for the study of QM tunnelling properties in the presence of intrinsic nonlinearities. To this end, there are two possible options, either we study the specific nonlinear coupling of a given case with all its peculiarities and details, as done in Ref. [14] for ET between quinones in the photosynthetic reaction center, or we study a skeletal model which contains the essential elements of the problem and try to draw general qualitative conclusions from its physical behavior. We shall adopt the latter view here to highlight a specific property of the tunnelling process in the presence of nonlinearities; i.e., the presence of hysteresis in a symmetric donor–acceptor ET system.

Davydov's approach to electron–lattice deformation coupling in biological systems [4] and its variants [15] lead always to an effective Hamiltonian of the nonlinear Schrödinger equation (NLS) type. The nonlinearity in the equation comes from a *hidden* adiabatic coupling to an external interaction (the deformation) which is factored out from the dynamics in the form of an effective self-consistent potential. The Hamiltonian is always of the *self-localizing type*, i.e., with a negative nonlinear potential. We have studied very recently two models with this property in the framework of the ET problem [16]. The simplest possible discrete symmetric donor–acceptor ET system, including a nonlinear coupling of the Davydov type, is

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