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Book Review: *Energy Landscapes: Applications to Clusters, Biomolecules and Glasses (Cambridge Molecular Science)*

Energy Landscapes: Applications to Clusters, Biomolecules and Glasses (Cambridge Molecular Science) by David J. Wales (Cambridge University Press, 2004).

David J. Wales' book *Energy Landscapes* is itself a description of a landscape, namely of the science of systems composed of a relatively small number of atoms or molecules in which disorder plays a crucial role. The understanding and mathematical properties of potential energy surfaces (PES) present an underlying unifying theme of this type of system. The book is written in the form of a treatise on the way dynamic and thermodynamic properties of various systems are encoded in, and can be deduced from, the features of their respective potential (or free) energy surfaces. It covers a whole slew of theoretical subjects introducing the concept and characteristics of PES and then going all the way to important applications in small clusters, biomolecules and glasses.

In many respects Wales' book defines a whole new subject, even more—a whole new field, and at the same time presents its state of the art description. It is very ambitious in its scope, extremely broad in its subject matter, and by necessity relatively uneven in its treatment. Nevertheless it is a superb and laudable achievement, and I believe it will represent a resource on the subject of PES for years to come.

With its onerous 692 pages and ten voluminous chapters with extensive and exhaustive lists of references, Wales' book is not an easy read. Though it is intended for nonspecialists, graduate students and advanced undergrads alike, I doubt that any part of the intended audience will be able to follow its broad strokes in their entirety. This does not mean it is a dull book. On the contrary. Wales manages to write in a very lively and engaging style that invites learning, while the really superb illustrations that abound in the book enliven his presentation and urge the reader to carry on. Though the encyclopedic breadth of the book might overawe an unprepared reader, I am sure it will eventually make its mark by being the resource on the subject of PES and their applications in various systems.

But what really fascinates me about Wales' book is its inherent interdisciplinarity stemming from its excursions into the worlds of nano and bio. It moves through a number of fields unifying them through the concept of PES. This is probably also its most important and lasting achievement. The author has mostly managed to strike a fine balance between the descriptive breadth of exposition and mathematical details of each of the subject matters. The book is thus not unmanageably technical and should be at least in part accessible to a fairly broad and wide ranging audience composed of physicists, physical chemists and molecular biologists, while helping them to realize the underlying unity between different contexts in which PES emerge as an important tool for understanding the dynamic and thermodynamic behavior of different systems.

I can certainly wholeheartedly recommend it as an exhaustive guide and treasure trove of resources in the fascinating worlds of PES. Though in its entirety it is probably not suited for an advanced undergraduate or even a graduate course, parts of it can serve as a very illuminating and helpful introduction not only to the field of PES itself but also as an introduction to the study of molecular clusters such as small water clusters, properties of biomolecules such as proteins and glassy as well as disordered materials in general. All in all due to its encyclopedic breadth, this book stands a bit off the beaten path, while remaining a laudable enterprise and a first class achievement.

The subject matter of this treatise is varied and broad. As stated, the nature of the exposition while not straying from some technical and mathematical fine points, remains within the bounds of accessible. The first chapter, the Introduction, states the motivation of the book: to present a unified and reasonably self-contained view of potential and free energy surfaces together with their use in the study of clusters, biomolecules, glasses and supercooled liquids. The structure and dynamics of atomic and molecular clusters, folding of proteins and phenomenology of glasses are all aspects of PES or FES. The most important features of PES are their local minima, the global minimum and different transition states, with various pathways between minima defined by the connectivity of the PES. The study of atomic and molecular clusters of rare gas atoms, molecules, metal and non-metal atoms, based on multilayer polyhedra is introduced as an example of the workings of PES. Levinthal's paradox as well as the phenomenology of proteins and protein structure with energy landscapes in protein folding are introduced as an additional example of the workings of PES. The dynamics, pressure effects and aging of glasses and supercooled liquids serve as the last example of the phenomenology of PES.

The second chapter is dedicated to the basis of the PES i.e. to the Born-Oppenheimer approximation (BOA) and normal mode analysis. BOA is fundamental to the introduction of PES since it allows us to ignore other degrees of freedom such as electronic coordinates and to concentrate on the configurations

of the molecules as a whole. This chapter deals with a formal mathematical introduction of BOA and its limitations together with some simple examples of PES and some of its basic properties such as PES crossings and its consequences.

Symmetry considerations are dealt with in the third chapter. Symmetry is a key player in the description and analysis of PES and is introduced through the not impenetrably technical essentials of the group theory. Molecular symmetry groups of rigid and non-rigid molecules and especially the polytetrahedral packing and the geometric description of packing in bulk systems is discussed through symmetry considerations.

Features of the landscape are dealt with in the fourth chapter with the same heading. The stationary points of the PES are introduced and analyzed in terms of local minima and transition states. The classification of the stationary states is based upon the properties of the matrix of the second derivatives (the Hessian matrix), especially its eigenvalues. Thus the transition state is defined as a stationary state with a Hessian that has a single negative eigenvalue and is connected to different local minima by steepest descent pathways. Branch points, geometrical symmetry selection rules, and (McIver—Stanton) symmetry transition rules are also introduced and explained as well in this chapter.

The following chapter is dedicated to a description of the landscape. In order to understand the features of PES, which is a 3N dimensional function where N is the number of particles, one needs to devise aids to facilitate visualizing the energy landscape. Two appropriate visualization aids introduced in this chapter are: monotonic sequences and disconnectivity graphs. The monotonic sequence is a sequence of local minima and correposnding transition states along which the energy constantly decreases. This concept also defines the basin or folding funnel—a sequence of states that leads to the same local minimum. On the other hand the disconnectivity graphs are defined as superbasins at a certain fixed value of energy such that PES pathways between them never exceed this fixed energy. Lennard-Jones clusters, C(60) fullerenes and Lennard-Jones polymers are discussed as examples of use of these visualization aids. Disconnectivity graphs can also be understood in terms of the small world networks.

The sixth chapter explores the landscape and is based on methods to locate and characterize different features of PES including the global minimum of the surface as well as higher index saddles that have more then a single negative eigenvalue. These methods include molecular dynamics (MD), Monte-Carlo simulations (MC) and stochastic dynamics together with various techniques of biased sampling.

The seventh chapter deals with properties of the landscape. Both dynamic and thermodynamic properties of the various systems can be obtained from the stationary points sampled from PES. The superposition approximation is especially valuable in this respect since it allows one to write the partition function in terms

of contributions from different local minima in the classical and quantum limit. An approach based on the master equation to dynamics through paths between different local minima and transtion states allows the use of the PES features in the dynamical context. This chapter also deals with and introduces the role of catastrophe theory in understanding the role that the features of PES play in dynamics and thermodynamics of various systems.

Chapter eight deals with various molecular or atomic clusters. It builds on the introduction to atomic and molecular clusters in the first chapter and proceeds with a more detailed description of the nature and properties of clusters. Finite size effects, thermodynamic stability and phase transitions of clusters are discussed in detail. Cluster simulations with Lennard—Jones interactions are used to introduce their structure and properties of the corresponding PES that can show, in the most simple version, a single or a double-funnel landscape. Cluster simulations with Morse interactions are used to discuss the importance of the range of interatomic potential that separates the Lennard—Jones from the Morse clusters in terms of thermodynamic and dynamic properties. Additional interesting examples of atomic and molecular clusters are the alkali halide clusters, the buckminsterfullerene and especially and most importantly water clusters which are discussed in considerable detail.

The ninth chapter is dedicated to PES in biomolecules. Biomolecules are in many respects quite similar to other molecular clusters. Computer simulations are used as a primary tool to understand and predict protein structure ab initio. More coarse-grained lattice and off-lattice models such as the random energy model are also used to understand features of protein structure such as frustration. Structure of various polypeptides and proteins is used as examples of protein PES in order to discuss the relation between the PES properties such as disconnectivity graphs and protein structure.

The subject matter of the last chapter is that of glasses and supercooled liquids. Apart from discussing the connection between the glass transition temperature and the features of PES this chapter introduces also some of the theories of the glassy state such as the free volume theory and the mode coupling theory of the glass transition. It also deals with models based on the spin glass theories, though spin glasses are quite different from ordinary glasses since they assume a regular lattice. Simulation of glasses and superposition description of glasses in terms of inherent structures as embodied by the PES is introduced next in order to connect the transition states and pathways between local minima in glasses with molecular rearrangement mechanisms.

Once again this is in many respects a beautiful, well conceived and most informative book. It moves elegantly and engagingly through various fields of theoretical physics, physical chemistry and molecular biology to expose and explain the unifying workings of the potential energy surfaces and along the way finds

an elegant and meaningful connection, on a most fundamental level, between the worlds of nano and bioscience in a way hardly attempted before.

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