The holographic principle for latent molecular properties

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Dedicated to the 80th birthday of Professor Frank Harary

All information about all latent molecular properties, not exhibited by a given molecular structure but reproducibly exhibited by the same molecule in a different state or having a different conformation, is fully encoded in any nonzero volume of the non-degenerate ground state electron density.

1. Introduction

Density functional theory has made spectacular advances in providing an intuitively transparent model and also computational tools for the study of molecular systems [1]. Whereas many of the computational techniques follow an engineering approach where justification for some of the actual approximation schemes applied comes from the observation that they "work", nevertheless, the results usually validate these approaches. On the other hand, one important achievement of density functional theory is the recognition of the fact that many tempting and popular analogies between classical and quantum models themselves require quantum mechanical interpretations. In this study we shall explore one aspect of such an analogy: how information is stored and processed by molecular electron densities, where the classical analogy of a material object that encodes information will be used, within the context of quantum mechanics.

One fundamental result of density functional theory is the Hohenberg–Kohn theorem [2]: the non-degenerate ground state electron density determines the energy (and, in fact, through the Hamiltonian, all molecular properties). For artificial, closed and bounded systems Riess and Münch have shown an important related result [3]: if the complete system is finite, with a closed boundary, then the Hohenberg–Kohn theorem applies to any closed and bounded subsystem of it, as long as the ground state electron

density is non-degenerate. Whereas real molecules are neither bounded nor finite in a rigorous sense, so the result of Riess and Münch is not applicable to actual molecules, nevertheless, it has motivated further analysis leading to fundamental relations and new developments [4–7].

Electron density and atomic nuclei are the only physical entities contained in molecules, and the electron density contains all information about the nuclei. Thus, on information-theoretical grounds the consequence of the Hohenberg–Kohn theorem [2], that the non-degenerate ground state electron density determines all molecular properties is a very natural idea: there is simply nothing else in a molecule that could be the carrier of any additional information to determine molecular properties. Hence, purely on information-theoretical grounds, electron density must determine all properties [4–8].

In fact, as it has been proven more recently, for non-degenerate ground state electron densities the Holographic Electron Density Theorem applies: *any nonzero volume part of the non-degenerate ground state electron density cloud contains all information about the molecule* [4–7]. In this study we shall explore some further properties of the molecular information, relevant to the so-called *latent properties*, not directly exhibited by the actual electron density, that, nevertheless, serves as the source of the information.

2.   Molecular electron densities and latent properties

In the proofs of the Hohenberg–Kohn theorem and the holographic electron density theorem some very natural properties of molecular electron densities have been assumed. Foremost among these assumptions are the very existence of a ground state electron density function and the assumption of continuity of this function in the space variable **r**. Here we shall not elaborate on the matter of time scale where such a density function appears justified, however, one should be aware of the effects of zero point energy and the associated vibrations which do, in fact, modify both the role of the effective external potential for electron density and the role of time. Electron density changes and fluctuations can carry information, and all constraints on this information are also dependent on the ground state electron density.

Consider a molecule *A* in its non-degenerate electronic ground state. Typically, many of the molecular properties exhibited by the isolated molecule *A* are those which are primarily associated with nuclear arrangements similar to the most stable one (typically, an energy minimum), and the electronic ground sate. These are the *exposed properties* which one may regard as those directly associated with the ground state electron density.

However, the same molecule also has properties which are not exhibited in the electronic ground state at the most stable conformation. A so-called *latent property P* of the molecule is one that is reproducibly exhibited by the molecule if it is exposed to a specific interaction, or to a specific range of interactions. These latent properties are those which are associated with electronic excited sates, with highly distorted nuclear arrangements, with different stable conformations, or even with products of dissociation

reactions preserving the same overall stoichiometry of the original molecule. A latent property P may be regarded as the response of the molecule to a specific interaction X.

3.   The Holographic Electron Density Theorem for latent molecular properties

One may ask the question: where is the information stored that determines all such latent properties? Clearly, many of these properties are exhibited in response to some interactions, and the interacting partner or partners must have a role in the manifestation of the latent properties. However, a different molecule has different latent properties and the process involving the same interaction partner or partners leads to a different set of latent properties. For example, the interaction with a photon of the same energy may, reproducibly, lead to the manifestation of well-defined but different latent properties for two different molecules.

The information content of the photon of a specific energy may be regarded as minimal; clearly, most of the information concerning latent properties must be stored within the molecule itself. In fact, in the case of the photon having a specific energy, the information external to the molecule provides only the selection, which latent property of the molecule (which electronic excited state with all its properties) is going to be exhibited. In this sense, all the essential information concerning the latent property must be stored in the molecule. The external information of the photon is used merely to convert some of the latent properties of the molecule into actually exhibited properties, that is, to select for exhibition some of the actual latent properties for which the information is already stored in the molecule.

Consider a molecule A of a non-degenerate ground state electron density $\rho(\mathbf{r})$, and a latent property P. This property P is not directly exhibited by the electron density $\rho(\mathbf{r})$, however P is reproducibly exhibited by the molecule A following a specific interaction X. If one regards P as a component of the response of A to the specific interaction X, then all information about this response must be stored within the molecule A. However, all information in molecule A must be stored within the electron density $\rho(\mathbf{r})$, and by virtue of the holographic electron density theorem, any small positive volume part of the electron density $\rho(\mathbf{r})$ must also contain this information. This proves the following.

Holographic Electron Density Theorem for latent molecular properties. Any small positive volume part of the non-degenerate ground state electron density $\rho(\mathbf{r})$ of any molecule A contains all information about any latent property P of the molecule, regarded as a component of a reproducible response of molecule A to a specific interaction X.

In fact, this theorem and the original holographic theorem can be combined into a single statement:

Any small, nonzero volume piece of the non-degenerate ground state electron density cloud of molecule *A* contains the complete information on all actual and all latent molecular properties of molecule *A*.

Apparently, positive volume parts of the electron density clouds contain a remarkable amount of information, in some sense exploiting their continuum nature: they encode all information concerning all actual and all latent properties.

4.   Some consequences

Based on the Holographic Electron Density Theorem for latent molecular properties, electron density stores information in a way that is very different from what has been commonly assumed. Not only the actual properties exhibited by the molecule are fully determined by any positive volume part of the electron density cloud, but all potential, reproducible responses of the molecule resulting from various interactions are also determined by any such part of the electron density.

For example, considering the properties exhibited in a given excited electronic state of the molecule as the molecular response to the interaction with a photon of energy precisely equivalent to the energy of excitation, the complete information about this response is already fully encoded within any nonzero volume part of the original electron density $\rho(\mathbf{r})$ of the molecule *A*.

Similarly, specific interactions leading to responses such as conformational variations, generation of transition structures requiring well-defined energy of activation, or in a broader sense, all the properties of potential energy hypersurfaces of all electronic states [9], all molecular shape properties [10], chemical reactivity, and biochemical activity [11] are all latent properties of molecules, fully determined by any small, nonzero volume piece of the non-degenerate ground state electron density cloud of molecule *A*. It appears, that this result may have applications in the emerging field of molecular-level informatics [12], assumed to provide a framework as well as tools of applications in research aiming at the development of supramolecular and molecular computers.

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