

Unexpected expectation values for latent molecular properties

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Abstract Latent molecular properties are not exhibited by the given molecular structure but are reproducibly exhibited by the same molecule in a different electronic state or if some molecular interactions have taken place. A consequence of the Holographic Electron Density Theorem, as applied to latent properties, provides a framework that allows an extension of the expectation value formalism, leading to “unexpected” expectation value expressions for latent properties. Connections of special cases of this approach to earlier density matrix extrapolation methods are pointed out.

Keywords Unexpected expectation values · Holographic electron density theorem · Latent molecular properties · Potential energy surface extrapolation · Conformational variations · Transition structures · Electronic excited states · Reactivity

1 Introduction

Various formulations of electron density representations have provided important insight into molecular properties, starting with early statistical models (see, e.g. [1–3]) and density functional theory [4–10], with a central role of the Hohenberg–Kohn Theorem [10].

As established by this important theorem [10] already in 1964, information on all molecular properties can be deduced, at least in principle, from the molecular

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electron densities (strictly speaking, the proof of the theorem establishes this only for non-degenerate ground state systems). Explicitly, the Hohenberg–Kohn Theorem states that in a non-degenerate ground state, the molecular electron density determines the molecular energy and all other properties. This may be stated differently: the molecular electron density carries the complete information about the molecule. Consequently, the Hohenberg–Kohn Theorem may be regarded as the fundamental theorem of Molecular Informatics.

Later related developments provided additional results. An important result, although not applicable to real molecules, only to artificial, bounded quantum systems confined to finite regions of the three-dimensional space, was achieved by Riess and Munch [11] in 1981. For finite and bounded model quantum systems with boundaries, their result established the following:

Any nonzero volume *part* of the non-degenerate ground state electron density of a closed and bounded model quantum system can be extended a unique way to the complete, although finite model quantum system.

Clearly, real molecules are not closed, neither finite nor bounded, they cannot possess boundaries, hence this result is not applicable to real molecules. Whereas the limitation of a finite and bounded model represented by a closed set may appear not too serious, it is, on the one hand, physically significant when contrasted to the open and boundaryless nature of real molecules, and on the other hand, for such artificial systems the formal mathematical treatment is simpler, precisely as a consequence of the physically unrealistic closed and bounded properties of the model. This very limitation was well recognized and was correctly treated by Riess and Munch [11], who did not overstate the scope of their result, and in fact, this limitation had a fundamental role in their proof. Note, however, that in general, ignoring such limitations is one of the possible pitfalls of careless application of some mathematical theorems. In fact, this is one of the two, nearly equally misleading false mathematical steps (“deadly sins in mathematics”), which are

1. division by zero, and
2. treating open systems as if they were closed systems.

Doing either 1. or 2., one may falsely claim to “prove” almost anything and the opposite, simultaneously (thereby achieving the ultimate “false democracy” of ideas, where every statement is lowered to the rank of mere “opinion”, or the ultimate “false democracy” of mathematics: “all numbers are created equal”).

Therefore, any attempt to find a similar local-global information relation for real molecules, had to take into account the additional mathematical difficulty of treating open, boundaryless systems.

As it turned out, by applying a four-dimensional transformation and exploiting some additional fundamental properties of molecular electron densities, it was possible to prove the following “Holographic Electron Density Theorem” (Mezey [12]) for the open systems of real, boundaryless molecules:

Any nonzero volume *part* of a molecular electron density in a non-degenerate ground state contains the *complete* information about all properties of the entire, boundaryless molecule.

2 Exhibited and latent molecular properties revisited

One extension [13] of the Holographic Electron Density Theorem involves the concepts of exhibited and latent molecular properties.

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

However, the same molecule M , or a system that can be obtained from it also has properties which are not exhibited in the electronic ground state at the most stable conformation of the original molecule M . A so-called *Latent Property* P of the molecule is a non-exposed property that is reproducibly exhibited by the molecule if it is exposed to a specific interaction, or to a specific range of interactions.

For example, some of the latent properties of the most stable conformation of ground state molecule M are those which are associated with the electronic excited states, or those of its highly distorted nuclear arrangements, or different stable conformations, or even with products of dissociation reactions preserving the same overall stoichiometry of the original molecule M .

A latent property P may be regarded as one consequence of the response of the molecule M to a specific interaction X .

It is natural to ask the question: where is the information stored that determines all such latent properties of a molecule M ?

Some of these latent properties are exhibited in response to some interactions, and it is evident that the interacting partner or partners must have some role in the manifestation of the latent properties. However, an essential part of the information must come from the molecule itself, since different molecules M and M' usually have different latent properties, and even a process involving the same interaction partner or partners for two different molecules M and M' is likely to lead to two different sets of latent properties.

A latent property may be one that is *an observable property for both the original and the modified molecule*, but the *observed values are different*.

Alternatively, a latent property may be one that is *not even well-defined for the original molecule*, but it is *well-defined for the modified molecule*.

An example for the latter case is the “latent dipole moment of a cation M^+ , that becomes exhibited after the cation receives an electron”. Here, at least in the traditional sense (although generalizations are possible), no dipole moment is interpreted for the cation M^+ , but a dipole moment is well defined for the neutral molecule $(M^+)' = (M^+)^- = M$ obtained by adding an electron. Still, a “latent dipole moment” of cation M^+ can be considered in such cases as well.

By an extension of the original holographic theorem, the latent molecular properties can also be included, leading to the Holographic Electron Density Theorem for Latent Properties (Mezey [13]), stating:

Any nonzero volume *part* of a molecular electron density in a non-degenerate ground state contains the *complete* information about all latent, non-exhibited properties of the entire, boundaryless molecule [13].

According to the Holographic Electron Density Theorem for Latent Properties, even local regions of the molecular electron density, possibly quite remote in 3D space from the actual molecular region primarily responsible for a given latent property, already carry the necessary information for the determination of the given latent property.

Latent property theory also raises several questions concerning the conventional view of similarity, since on an information-theoretical basis and invoking some of the tools of complexity theories, the fundamental information content in the actually present molecule and the one already exhibiting the previously only latent properties is nearly invariant, where “near invariance” can be interpreted by measure theory and the “measure zero” concept.

These results imply that local electron densities can be used for latent property prediction.

By the inclusion of latent molecular properties to the family of properties which can be studied in terms of molecular fragments, the conventional tools of molecular similarity analysis, for example, those based on the tools of the quantum similarity methodology of Carbo and several related approaches [14–24], can be effectively employed in a much wider context.

3 A formal extension of the expectation value concept for latent properties

The concept of expectation value is a central concept of quantum mechanics concerning observables and the measurement process. For linear Hermitian operators A representing observables, with respect to a wavefunction Ψ , the definition is

$$\langle \Psi | A | \Psi \rangle = X, \quad (1)$$

that gives the actual eigenvalue X of wavefunction Ψ if it is an eigenfunction of operator A , where X corresponds to the resulting value obtained by measurement, otherwise X is the average value of infinitely many measurements performed simultaneously on infinitely many identical physical systems all described by the same wavefunction. Clearly, this second case cannot be verified by experiments, nevertheless, all the known facts appear to confirm the validity of this definition.

The above interpretation for the second case, by the very definition, is usually considered for “exhibited properties”. However, one might argue that the above second case in fact corresponds to possibly infinitely many latent properties, since the measurement can cause the non-eigenstate system to change in a way that cannot be predicted, and the results of individual measurements are for actual properties for infinitely many systems, possibly different in various ways from the original system. Hence, even the original expectation value concept can be viewed from the perspective of latent properties.

However, one may consider the problem of latent properties with respect to specific changes of the original molecule M to some system M' , where the originally latent property of M is an exhibited property of system M' .

Whereas the electron density approach provides an important framework for latent properties in terms of the Holographic Electron Density Theorem for Latent Properties, note, however, that the traditional wavefunction approach also holds advantages, especially, for property predictions, and latent properties are exceptional in this context as well. In fact, the wavefunction approach for latent properties leads to some “Unexpected Expectation Values”.

One may start out with the natural assumption that various wavefunctions, such as those of the original and modified molecules, can be converted to one another. Consider a latent property that is not exhibited by a molecule M of wavefunction Ψ , but after some interaction, the molecule changes to M' , now described by wavefunction Ψ' , and the modified molecule M' already exhibits a property X' that is originally only latent property for molecule M . This property X' can be expressed as the expectation value

$$\langle \Psi' | A | \Psi' \rangle = X', \quad (2)$$

where the traditional concept of the expectation value is used.

If C is an operator that has adjoint C' , where operator C , when acting on the molecular wavefunction Ψ of M converts it to wavefunction Ψ' of the modified molecule M' , that is, if

$$C \Psi = \Psi', \quad (3)$$

then using the operator A corresponding to the measurable property X' gives the expectation value

$$\langle \Psi' | A | \Psi' \rangle = \langle \Psi | C' A C | \Psi \rangle = X', \quad (4)$$

that is in fact a formal, “unexpected” expectation value of operator $C' A C$ with respect to the original wavefunction Ψ , for a property X' that is not an exhibited property, only a latent property with respect to the corresponding original molecule M .

The above “unexpected” expectation value relation for the original wavefunction Ψ ,

$$\langle \Psi | C' A C | \Psi \rangle = X', \quad (5)$$

when compared to the representations of local electron densities and some of the similarity concepts, leads to similar applications as the ordinary expectation values commonly used for exhibited properties.

We may say that, the operator $C' A C$ takes the role of the operator for a formal “latent observable property” for system M described by the wavefunction Ψ , where the property corresponding to operator A , belongs to an actual observable for system M' described by wavefunction Ψ' . The very same operator A may give a different

value for this observable, if applied directly to the wavefunction Ψ for system M, or possibly, operator A does not even belong to an actually observable traditional property for system M.

In effect, the family of observables for system M is extended by a family of “latent observables”, with the corresponding operators of type $C' A C$, where the same expectation value formalism can be applied as usually applied for the actual observables.

Note, however, that the transformation operator C, converting wavefunction Ψ to Ψ' can be rather complicated, and the new operator $C' A C$ may violate some of the usual requirements of quantum mechanical operators associated with observable properties. Specifically, linearity may no longer apply, and a computational determination of C may be complicated in various cases. Also note, however, that some of these limitations are expected, since if all the usual requirements for quantum mechanical operators commonly associated with observable properties would be fulfilled, then the very property would no longer be considered a latent property, but an exhibited property, one, that in such a case would be just a member of the family of the observable properties of the original system M.

It is worthwhile to point out that, extrapolations along potential energy hypersurfaces are common cases for latent property predictions, for example, those extrapolations along reaction paths [25]. In such cases, one might prefer some density functional or density matrix formalism instead of the use of formal expectation values, especially, if sufficient accuracy can be achieved with simpler approximate methods.

4 Summary

By invoking an operator C converting the wavefunction Ψ of a molecule M to a wavefunction Ψ' of a modified molecule M' that has an exhibited property of operator A which is only a latent property for the original molecule M, a formal, expectation value expression can be constructed, directly involving the original wavefunction Ψ and a transformed operator $C' A C$.

With such operators $C' A C$ of “Latent Observables”, belonging to “Latent Properties” with reference to system M of wavefunction Ψ , some “Unexpected Expectation Values”

$$\langle \Psi | C' A C | \Psi \rangle = X'$$

can be obtained, *all within the usual expectation value formalism.*

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