A simple truth hidden in plain sight: All molecules are entangled according to chemical common sense

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Abstract:

An equation that determines the numbers of electrons for molecules is proposed based on chemical common sense. It shows that all molecules are entangled in number of electrons and results in the fundamental assumption of molecular energy convexity that underpins molecular quantum mechanics. It also leads to the concept of fractional numbers of electrons for molecules in a statistical sense. The energy of a molecule is piecewise linear with respect to its continuous number of electrons. Wavefunction interpretation of this equation of nature shows that an individual molecule with noninteger number of electrons is locally physical, whereas a molecule with integer number of electrons is locally real. The complete theoretical proof of the equation is still to be had.

Molecular size consistency principle[1] is routinely used in molecular quantum mechanics to measure the correctness of approximate methods. It states that, given two molecules A and B, the internal energy[i] of a system made of A and B separated by a very large (e.g., visible) distance is the sum of the internal energies of X and Y:

$$E(A..B) = E(A) + E(B) \tag{1}$$

We use '..' to indicate a visibly measurable distance. We call this type of separation *asymptotic* henceforth. The validity of this principle is obviously based on the following commonly held believes and observations by molecular scientists:

1. Matters are dividable. Specifically, they are divided into molecules (with atoms as special cases).
2. Molecules have one definite, time-independent internal energy because chemical reactions produce energy changes. This singleness of molecular energy is of cause relative to a constant reference value for all molecules.
3. Thermodynamically stable matters visibly separated from each other are independent of each other with the omission of magnetic and gravitational interactions.

All the above points can be summarized as stating that molecules are locally real[ii] in energy.

We define *chemical common sense* as a collection of commonly held believes or observations among practitioners of molecular sciences in humans' sense of space and time at a normal range of temperature. Eq.(1) is perhaps the most concise way to quantitatively formulate the basic chemical common sense listed above. It projects properties at macroscale (i.e., many molecules) to the properties of molecules at microscale (i.e., individual molecule). Some well defined approximate quantum methods yield different results when applied to the LHS and the RHS of Eq.(1), indicating their incorrectness. However, the impact of this principle of nature has been limited to being a criterion for the correctness of approximate methods, perhaps due to its obviousness and lack of significant derivatives.

We very recently derived[2] a more general relation for electrons between two asymptotically separated molecules based on density functional theory (DFT)[3-5]:

$$E((X..Y)_L) = \min_N (E(X_N) + E(Y_{L-N})) \tag{2}$$

Here, $(X..Y)_L$ symbolize a molecule with two asymptotically separated sets of nuclei X and Y and L number of electrons. X_N is a molecule with a set of nuclei X and N number of electrons. The relative positions of nuclei are fixed. L is a positive integer and N a positive real number. The minimizer is unique in the sense that N^* is either a single integer or between two consecutive integers. It satisfies the following conditions[iii]:

$$I(X_{\lceil N^* \rceil}) \geq A(Y_{\lfloor L-N^* \rfloor}), \quad A(X_{\lfloor N^* \rfloor}) \leq I(Y_{\lceil L-N^* \rceil}) \tag{3}$$

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[i] All molecular energies are assumed to be for ground states.

[ii] An object is said to be *local* if it is defined within a limited spatial range in 3-D. A property is said to be *local* if it belongs to a local object and determined by the surroundings of the object within a limited 3-D range. An object or property is said to be *real* if its existence or value is independent of measurements. All classical particles are considered locally real.

[iii] $\lceil N \rceil$ (ceiling) is the smallest integer not smaller than N. $\lfloor N \rfloor$ (floor) is the largest integer not larger than N.

where A and I stand for vertical electron affinity and ionization potential, respectively. The values of A and I are defined based on the definition of the energy of a molecule.

Eq.(2) has a simple physical meaning: two molecules will exchange electrons to lower the total energy, which determines the number of electrons of each molecule. The determined number of electrons may be noninteger when an electron can be transferred without causing energy change. The existence and the uniqueness of the minimizer of Eq.(2) is ensured by the assumption of molecular energy convexity (MEC)[6], which states that $I(X_L) > A(X_L)$, i.e., the ionization potential decreases as the number of electrons increases.

The size consistency principle is a special case of Eq.(2) for $N = N^*$ with N^* being an integer. This shows that the two molecules on the RHS of Eq.(1) are *not* locally deterministic as it appears. In practice, the number of electrons for a molecule can often be correctly guessed based on the electron affinity and ionization potential data, which is equivalent to a manual application of Eq.(2). Molecules in nature are typically neutral due largely to the fact that the smallest ionization potential is larger than the largest electron affinity in the periodic table. But some molecules, such as superalkali, have ionization potentials as low as 3.51ev[7], which is lower than the electron affinity of chlorine. It is also theoretically possible to prepare a stable ion in a controlled environment if the ion and its container satisfy Eq.(3).

In this article, we attempt to establish Eq.(2) as a rule of chemical nature independent of how the energy is formulated. By 'rule of chemical nature', we mean that it is derivable from some basic chemical common sense, is concise, has essential and critical consequences, and is not derivable from other laws/theories at the current level of knowledge in literature. In particular, we show that the new equation has these important derivatives: (1) It shows that locally real molecules are entangled in number of electrons; (2) It results in MEC; (3) The energy of a molecule is piecewise linear with respect to its continuous number of electrons if the number of electrons were to be extended to being fractional.

We first add the following to the list of the basic chemical common sense:

4. Molecules are made of atoms, and atoms are made of negatively charged electrons and positively charged nuclei with integer charges concluded from J. J. Thomson's experiment in 1897. Individual electrons and nuclei are indivisible. Electrons are transferable between molecules accompanied by energy variation.
5. Electrons do not hold stable local structures on their own because there is no stable net charge accumulation at the macroscale that we can detect. This is also consistent with the singleness of molecular energy. In contrast, nuclei can have stable local structural arrangements because we see matters have variations.
6. Electrons are always near nuclei spatially because we do not catch electrons floating in air by themselves.
7. The energy of a molecule is nonlinear with respect to its number of electrons, i.e., ionization potential is different from electron affinity. Otherwise, we would observe zero net change of energy for electron transfers between separated molecules.
8. The variational principle is applicable to the energy of a molecule regardless how it is formulated.

We propose that Eq.(2) with integer N 's is the most concise quantitative formulation about electronic movement in molecules that can be deduced from the chemical common sense stated above:

- It includes the molecular size consistency principle.

- The energy of a molecule is a function of its number of electrons since the variation of this number involves change of energy. It is not a function of electronic positions because of the singleness of the molecular energy. This validates the expression $E(X_L)$.
- The requirement of integer N 's shows the indivisibility of electrons.
- Minimization is the application of the variational principle.
- The singleness of the minimizer is due to the singleness of molecular energy and the nonlinearity of molecular energy with respect to the number of electrons.
- There is no need for additional terms on the RHS because electrons are always with nuclei spatially.
- It is time-independent due to the stability of molecules.

The molecule on the LHS of Eq.(2) is assumed to be *alone* in the universe[iv]. The molecules on the RHS are said to be *open* because they can exchange electrons with each other. The equation implies a critical assumption that the energy of an open molecule asymptotically separated from others is defined as if being alone. It stems from the common sense that molecules are locally real in energy. Furthermore, we observe that electrons in the equation are treated as being locally real as part of a molecule in an asymptotic sense with one exception: Unlike forces between particles in Newtonian mechanics that diminishes over distance, the determination of the local parameter N is independent of the intermolecular distance beyond the asymptotic separation. In other words, *all molecules in the universe are entangled*[v] *in number of electrons*. This is a result of the singleness of energy and the openness of all molecules. The nonlocality in determining N means that the molecule X_N is locally deterministic only conditionally. This entanglement is not unusual if one thinks of $E(X_L)$ and L as variables for a collective state of electrons in analogy to the state variables of classical thermodynamics, where open systems interact distantly.

We can now derive MEC based on the sameness of energy for a molecule between open and being alone. Let us assume the opposite is true, i.e., $E(X_{K-1})+E(X_{K+1})\le 2E(X_K)$ with an integer K for a certain X. Applying Eq.(2) to the molecule $(X..X)_{2K}$, it would mean that $N=K$ would be either a local maximum or the system has the same energy for $N=K-1,K,K+1$, both of which violates the single minimum requirement. A local maximum leads to multiple minima, which would mean stable variation of net charge distributions. The sameness of energy would mean zero net change of energy for electron transfers between separated molecules.

We note that MEC is an important discovery[6]. It is a condition assumed in every molecular quantum mechanical calculation without being explicitly stated. Without it, the energy of the ground state of a molecule could have an energy higher than the energy of an ensemble of states with different numbers of electrons, which would throw all the calculation results in doubt. It is quite remarkable that an equation based on observations at the macroscale would predict such a consequential property at the microscale.

MEC leads to an obvious albeit nontrivial conclusion: Every molecule in a system made of asymptotically separated K sets of the same nuclei X with total $L\times K$ number of electrons has L electrons. This is to say that each individual molecule is the same as the average molecule. What if the

[iv] We consider the universe being made of molecules only.
[v] An object is said to be *entangled* if it is local and possesses a property that cannot be determined by locally measurable forces.

total number of electrons is not a multiple of K, e.g., a system made of many H^+ and H? To include such a scenario for Eq.(2), it is convenient to define an average molecule that has fractional number of electrons with the averaged energy, and N in the equation is now extended to being real positive. $E(X_N)$ *must be piecewise linear with respect to* N because net charges would accumulate everywhere otherwise, which is against the chemical common sense. This completes the formulation of the rule of chemical nature manifested by Eq.(2) describing the electrons of an averaged molecule.

The averaged molecule was used as the physical basis for fractional charge for molecules in the seminal work on the topic [6, 8]. Such a justification was criticized recently [9] for the reasons that an electron is physically indivisible and that a wavefunction solution for a molecular system requires an integer number of electrons. It is clear from the above discussions that there is no difference in physical reality between an averaged molecule with integer number of electrons and an averaged molecule with a noninteger number of electrons within the consideration of the chemical common sense where all the physical measurements are at macroscales and thus inherently averaged. On the other hand, it is logical to assume that an averaged molecule with integer number of electrons is as locally real as an individual molecule due to the MEC condition whereas an averaged molecule of noninteger number of electrons is apparently hypothetical.

We show that individual molecules with noninteger number of electrons are locally physical[vi] albeit not locally real when wavefunction theory is applied to Eq.(2), based on the standard treatment of physical measurements in quantum mechanics. Application of Born-Oppenheimer approximation to a molecule separates the electronic motion from the nuclear motion, with positions of nuclei being certain. Entanglement experiments have verified that the wavefunction of a pure state can be ubiquitous and a local physical measurement of the state is a local collapse of that global wavefunction. The result of a measurement is from a mixed state of all possible local pure states. This mixed state is entangled with the mixed states at other locales as part of the same global pure state. In the case of Eq.(2), the electronic wavefunction for the LHS spans over the two sets of nuclei. The RHS represents two measurements of energy at locales X and Y, respectively, and the detected mixed state at each locale is an ensemble of states with different integer numbers of electrons at that locale. This fluctuation matches exactly the openness of a molecule dictated by Eq.(2). The mixed states of the two open molecules are entangled as part of the pure state for the molecule on the LHS with a definite number of electrons. Furthermore, the wavefunction for the LHS must result in a distribution of electron density that conforms to the optimized numbers of electrons at those two locales. When N^* is a single integer, the mixed state at each locale coincides with a pure state for the molecule at the locale because MEC guarantees that the energy of the pure state is lower than any mixed state. On the other hand, the fact that the wavefunction of this pure state is the same as calculated of the molecule being alone does not mean the molecule is alone physically. When N^* is fractional in a range, $X_{N^*}..Y_{L-N^*}$ is degenerate with respect to the variation of N^* from $\lfloor N^* \rfloor$ to $\lceil N^* \rceil$. The measured energy at the locale X changes linearly such that the total energy remains the same with respect to the variation of N^*. One can see that the possibility of fractional number of electrons is a consequence for molecules being open for electron exchange as stated by Eq.(2)

[vi] An object or property is said to be *physical* if it is a real observable, or is derived with logical necessity within laws and theories of physics, as opposed to being an optional concept for convenience. Being real means being physical, but the opposite is not necessarily true per wavefunction theory. For example, the polarization of an entangled photon is not locally real but still physical; an averaged molecule of noninteger number of electrons as prescribed here is not physical because a logical division of a system of locally real molecules does not result in such a molecule.

and supported by wavefunction theory. Since all molecules in the physical world are open, individual molecules of noninteger numbers of electrons are just as physically valid as molecules of integer ones. A molecule with noninteger number of electrons differs from one with integer number of electrons in that its number of electrons fluctuates with repeated measurements, i.e., it is not locally real but still physical. The fact that the fluctuation of numbers of electrons is not typically encountered for stable molecules is a reflection of the physical rarity of the equalities in Eq.(3). An open molecule of integer charge can be treated as if being alone since its wavefunction stays the same, but only *after* the number of electrons is determined from the solution of the wavefunction of the universe. In short, *all molecules are also quantum-mechanically entangled in number of electrons.* We note that an entangled molecule of noninteger number of electrons is conceptually different from an averaged molecule even though local measurements cannot distinguish the two.

For wavefunction theory to be applied directly to each molecule on the RHS of Eq.(2), the stipulation in the equation that the sameness of energy between an open and lone molecule is needed. DFT, derivable from wavefunction theory, is more convenient in the sense that the energy is a functional of density, a locally real property. We showed recently [2] that the exact universal functional of integer number of electrons is extendable to being of fractional number of electrons, i.e., it can be written as $F_{UN}[N,\rho_N]$ where ρ_N symbolizes an electron density that integrates to N. The energy of a molecule calculated with the functional is locally deterministic. $F_{UN}[N,\rho_N]$ is asymptotically local:

$$F[N_X+N_Y,\rho^{(X)..(Y)}_{N_X..N_Y}]=F[N_X,\rho^{(X)}_{N_X}]+F[N_Y,\rho^{(Y)}_{N_Y}], \tag{4}$$

where $\rho^{(X)}_{N_X}$ symbolizes an electron density located in the region X. $\rho^{(X)..(Y)}_{N_X..N_Y}\equiv\rho^{(X)}_{N_X}+\rho^{(Y)}_{N_Y}$ is a density composed of densities from two asymptotically separated regions. This type of locality was named i-local ('i' stands for interaction.). Applying F_{UN} to $(X..Y)_L$ results in Eq.(2) with the aid of MEC. The DFT energy for a given number of electrons at each locale on the RHS of Eq.(2) corresponds to the energy of a local mixed state.

One may wonder if Eq.(2) is fully derivable from wavefunction theory. The answer is 'Not yet'. Our DFT-based derivation relied on the MEC assumption[2]. The latter is specific to Coulombic nature of interelectronic interaction and has not been proven theoretically[5, 10]. To prove MEC, one needs to show that the ground electronic state of a lone molecule of integer number of electrons is not an ensemble of states with different numbers of electrons, which is equivalent to say that the electronic energy of a lone molecule does not change when the molecule becomes open to electron exchange, i.e., a molecule with nonlocally determined integer number of electrons is locally real.

Lastly, we note that a molecule with noninteger number of electrons can obviously be placed at the LHS of Eq.(2). This raises a question: Can such a molecule be alone? The answer is No because an electron is indivisible physically, although its energy can be computed separately. Indeed, the separability of molecules shown in the RHS is considered an asymptotic property with wavefunction theory because the electron density of any molecular system never reach exact zero anywhere in space[11].

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