Dramatic changes in electronic structure revealed by fractionally charged nuclei

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Abstract
Discontinuous changes in the electronic structure upon infinitesimal changes to the Hamiltonian are demonstrated. Remarkably, these are revealed in one and two electron molecular systems if the realm of the nuclear charge is extended to be fractional. Dramatic changes in the electron density from full configuration interaction are observed in real space illustrating key intricacies of electronic structure including the transfer, hopping and removal of electrons. Physically, this is due to the particle nature of electrons and manifests itself theoretically as a diverging linear density response function or an energy derivative discontinuity that occurs at constant number of electrons. This is essential to correctly describe real physical processes, from chemical reactions to electron transport and metal-insulator transitions. The dramatic errors of DFT are seen in real space as this physics is missing from currently used approximations and poses a great challenge for the development of new electronic structure methods.

I. INTRODUCTION

How electrons move upon a change in the external potential, \( v(\mathbf{r}) \), is a key question in the understanding of the quantum nature of electrons in matter, given by the Schrödinger equation

\[
\left( \sum_i -\frac{1}{2} \nabla_i^2 + v(\mathbf{r}_i) + \sum_{i \neq j} \frac{1}{r_{ij}} \right) \Psi = E \Psi.
\]

A deeper understanding of the basic behaviour of electrons is needed and is the focus of this work. The change in \( v(\mathbf{r}) \) in processes such as stretching bonds, chemical reactions and electron transport is a great challenge for electronic structure theory. Methods such as Hartree-Fock (HF) and MP2 work well for many properties such as equilibrium structures, where the electronic structure is dominated by a single determinant, however they break down when the basic description of the wavefunction needs more than one determinant. Currently, the only way to tackle this challenge is with multi-reference wavefunction methods leading to an exact diagonalization of the full Hilbert space with Full Configuration Interaction (FCI) \([1]\), where the limitation is the exponentially scaling size of the space. Density Functional Theory (DFT) attacks the same problem in a fundamentally different manner using the real-space electron density Functional Theory (DFT) as it is based on the particle nature of electrons, whereas DFT relies on approximations to the exchange-correlation functional which breaks down when the basic description of the electronic structure is dominated by a single determinant, well for many properties such as equilibrium structures, where the electronic transport is a great challenge for electronic structure theory. Methods such as Hartree-Fock (HF) and MP2 work well for many properties such as equilibrium structures, where the electronic structure is dominated by a single determinant, however they break down when the basic description of the wavefunction needs more than one determinant. Currently, the only way to tackle this challenge is with multi-reference wavefunction methods leading to an exact diagonalization of the full Hilbert space with Full Configuration Interaction (FCI) \([1]\), where the limitation is the exponentially scaling size of the space. Density Functional Theory (DFT) attacks the same problem in a fundamentally different manner using the real-space electron density as the fundamental variable, with all the complexity now hidden in the exchange-correlation functional \( E_{xc}[\rho(\mathbf{r})] \). The same functional has to correctly describe all systems, i.e. the result of the functional on many systems is equivalent to many FCI calculations. The simplest example that this is a non-trivial problem is the incapability to make one functional that describes the energy of both stretched \( \text{H}_2^+ \) and stretched \( \text{H}_2 \) \([2]\). From a FCI perspective these two systems are trivial as they have one and two electrons, however in DFT it is the use of the same functional that links them (and in fact all other systems) together that poses a distinct challenge.

The connectedness between physical systems is investigated in this work by taking the normal external potential for a set of nuclei \( \{A\} \) at positions \( \mathbf{R}_A \) with charge \( Z_A \),

\[
v(\mathbf{r}) = -\sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|},
\]

and simply extending the realm of the charge of the nuclei from the usual integers, \( Z \in \mathbb{Z} \) to now be fractional, \( Z \in \mathbb{R} \). Fractional nuclei have been used previously in different contexts, from alchemical changes \([3, 4]\) to inverse-design \([5, 6]\) to QMMM evaluation of pKa \([7]\) to density of atoms \([8]\).

Here, the idea is used to give a simple and physical controllable change to the Hamiltonian such that, as theoreticians, a fine control over the electronic structure problem is achieved. It should be noted that only the external potential is changed such that electrons retain their nature, hence all electronic

![Figure 1: HZ(1+) : two protons with one electron, and varying the charge of one of the protons, 0 ≤ Z ≤ 2. The density is shown for (a) Exact and (b) PBE for three charges on the Z atom (0.99,1.00,1.01). The exact behavior shows very discontinuous behaviour at Z = 1 that a functional such as PBE fails to capture due to delocalization error. In (c) and (d) the same is illustrated but showing the whole range 0 ≤ Z ≤ 2, the curves in black correspond to the density for the integer points: H atom, H+ and HHe2+.](image-url)
structure methods should apply. Other physically motivated ideas such as model hamiltonians \cite{9} like the Hubbard model or Anderson model are different in that they also change the electron-electron interaction and, for example, conventional DFT functionals cannot be directly applied.

The exact behavior of electrons in some interesting but simple model systems is now investigated using these fractional nuclear charges. Exact calculations using full configuration interaction calculations (FCI)\cite{10, 11} are carried out and the behavior of the electron density $\rho(r)$ is examined. This reveals basic intricacies of electronic structure and fundamental behavior of electrons that can be seen in real space. This approach is applied to several simple examples with one and two electrons that are able to reveal fundamental challenges of describing the intricate nature of the quantum mechanical behavior of electrons. Remarkably, the visualization of dramatic changes in the density associated to the integer nature of electrons emerge and are possible to visualize in simple systems only with the use of non-integer nuclear charges.

First consider the $H_2^+$ molecule with two protons and one electron. From a wavefunction perspective this molecule is trivial as it only has one electron and Hartree-Fock gives the exact solution. However, it still offers an interesting and challenging behavior that can be illustrated by the failure of non-wavefunction methods such as DFT, which with LDA or GGA functionals upon stretching give a massive error in the energy of around 60 kcal/mol. This is the classic problem of self-interaction \cite{12, 13} or delocalization error \cite{14} in DFT. All semi-local functionals have a qualitative failure in the energy at infinity, however, the density is not qualitatively wrong, as it is constrained by symmetry to give half an electron on each end. In Fig. 1 we use fractional nuclei to turn this error in the energy into an error in the density. The charge on one of the protons (now called Z) is changed and allowed to be non-integer. The number of electrons is always fixed, constant at 1, hence this molecule is called $HZ^{1(e)}$. The exact behavior from FCI is very simple and clear at infinite separation of H and Z. For any $Z < 1$ all the electron is on the H (with corresponding energy $−\frac{1}{2}$) and for $Z > 1$ all the electron is on the Z (with corresponding energy $−\frac{Z^2}{2}$). For the point at $Z = 1$ (corresponding to $H_2^+$) the electron can be found half on the H and half on the Z. Thus, the exact behavior of the electron density is discontinuous with respect to $Z$ at $Z = 1$, clearly exhibiting the integer nature of electrons. It is found that an infinitesimal change in the Hamiltonian produces a dramatic change of the electron density. This can be compared to the performance of a typical GGA functional such as PBE \cite{15}. The density for non-integer $Z$ reveals the delocalization error in a very visual manner. Thus, the error for the energy of infinitely stretched $H_2^+$ is turned into an explicit error for the density in $HZ^{1(e)}$. PBE clearly misses the discontinuity at $Z = 1$ and favors a smooth charge transfer that leads to an over delocalized electron density that is on both H and Z. It is the first time that the delocalization error is visualized in such a clear manner in a real space picture of a one-electron system.

This simple exercise is highly illustrative of the complexity of electronic structure that occurs even in one-electron systems. There have been many previous papers on $H_2^+$, including many which have highlighted qualitative failures of the energy of DFT functionals, but none of them have focused on such an error in the density. It should be noted that the corresponding “chemical” change (with no fractional nuclei), going from $H_2^+ → HHe^{2+}$, does not illustrate this failure as the error of functionals is dwarfed by the difference in energy of the electron being on the two different atoms. From a density functional perspective the qualitative failure is a consequence of the delocalization error, that can be easily seen in real space. The delocalization error in DFT implies massive

![Figure 2](image-url)
failures in both the energy and the electron density. From a chemical point of view, this shows the particle nature of the electrons. This key aspect is missing from currently used approximations in DFT.

Next consider the simplest possible chemical reaction with three protons and one electron, $\text{H}_2^+ + \text{H}^+ \rightarrow \text{H}^+ + \text{H}_2^+$. For simplicity, a linear geometry is taken, with two protons fixed 10 Å apart and another proton moving between them. A 1-dimensional coordinate, $R$ (distance to the left proton), describes the reaction. For $R=1.0$ Å the electron is near the left proton and for $R=9.0$ Å the electron is near the right proton. Therefore, as the central proton moves from the left to the right the electron will be transferred as well. We also consider changing the charge on the central proton to be fractional, giving a reaction $\text{HZ}^{[1e]} + \text{H}^+ \rightarrow \text{H}^+ + \text{Z}^{[1e]}$. Fig. 2(a) illustrates the hydrogen atom transfer reaction with a charge $Z=1.0$. The density plots show how the electron is carried on the central proton as it moves from left to right. However, with a charge $Z=0.9$ on the central proton the reaction exhibits a completely different mechanism (Fig. 2(b)) proton transfer followed by electron transfer. Here, as the central proton moves $1 \lesssim R < 5$ the electron stays on the left H atom. This can easily be understood from the previous example, $\text{HZ}^{[1e]}$, where the stretching leaves the electron on the H. However, for the same reason, when $R > 5$ the electron is on the right H atom. Therefore, there is an electron hopping as $R$ goes through the midpoint, $R=5$. This is a very striking example of a conical intersection again showing how a very small change to the system leads to markedly different behavior of the electrons. Electronic structure methods must be able to describe all of these mechanisms correctly to provide a full understanding of chemical reactions and electron transfer processes. The performance of GGA methods for these reactions is disastrous due to delocalization error, with the electron spread over all three centers and a corresponding unphysical drop in energy.

Let us now consider closed-shell systems with two electrons. We first study the HZ$^{[2e]}$ system as the nuclear charge on the Z is varied from 0 to 2. This connects smoothly from H$^-$ to H$_2$ and to HHe$^+$. At stretched geometries these three integer cases have different occupations on the Z atom, with 0, 1, and 2 electrons respectively. The occupation of the Z atom $\langle n_Z \rangle$ (calculated by a simple Mulliken atomic population) is plotted in Fig.3 as a function of the charge on the nucleus Z at three different geometries: around equilibrium (0.75 Å), moderately stretched (2 Å) and further stretched (10 Å). The transfer of electrons as a function of Z is different in the three distance regimes. Restricted Hartree-Fock is able to describe the smooth transfer that occurs at shorter distances but fails qualitatively in the stretched limits to give any discontinuous behavior associated to electron hopping. The same is true for any DFT method that misses the derivative discontinuity. It does not give a step like behavior in the occupation $\langle n_Z \rangle$ and hence it does not correctly describe the integer nature of electrons in such electron transfer processes. This movement of electrons encapsulated in HZ$^{[2e]}$ is equivalent to that seen in the classic Anderson model of electron transport [15] [17], however it offers a much simpler connection to usual chemical concepts (real electrons and nuclei in 3-dimensional space) such that, for example DFT approximations can easily be applied and tested.

Our model systems illustrate examples where an infinitesimal change in the external potential leads to a drastic change in the electron density. This can be considered from the perspective of the linear density response function at constant number of electrons

$$
\chi(\mathbf{r}, \mathbf{r}') = \left( \frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right)_N
$$

In most physical situations a small perturbation of the Hamiltonian produces a small change in the electronic structure, however these cases show interesting phenomena where a small perturbation, for example changing the nuclear charge around $Z=1$ in the case of HZ$^{[1e]}$ or a movement in the geometry in HZH$^{[1e]}$ or a change in nuclear charge around $Z=0.3$ or $Z=1.7$ in stretched HZ$^{[2e]}$ lead to dramatic changes in the electron density. In these situations the linear response function, $\chi$, diverges. This is a challenge for approximate theories [18] as, for example, it is a priori natural to think that a diverging $\chi$ would be very difficult for a smooth differentiable functional of the density to reproduce. However, it is shown here that in the one electron examples an exchange-correlation functional such as Hartree-Fock or even a functional equal to the negative of the Coulomb energy, $E_{\text{xc}}[\rho] = -J[\rho]$, correctly describes a diverging linear response function. Of course any form such as LDA or GGA do not reproduce the correct behavior or indeed any sort of divergence of $\chi$. Another related second order response property is the Fukui function for electron removal, $f^-(\mathbf{r}) = \left( \frac{\delta \rho(\mathbf{r})}{\delta N^-} \right)_N(\mathbf{r}) = \rho^N(\mathbf{r}) - \rho^{N-1}(\mathbf{r})$, which
that for the case of $\text{HZ}^{(2e)}$ connects together the densities of $\text{HZ}^{(2e)}$ and $\text{HZ}^{(1e)}$. The $f^{-}(\mathbf{r})$ around $Z=1$ shows interesting and challenging behavior as even though the density (and hence orbitals) for $\text{HZ}^{(2e)}$ have a smooth behavior with no interesting features around $Z=1$, the Fukui function shows up a clear discontinuous behavior due to the discontinuity in the density in $\text{HZ}^{(1e)}$ which is not captured by the orbitals. Again the usual derivative expression for the Fukui function fails completely with currently used functionals, as they are missing the derivative discontinuity.

Finally we look at the electronic structure in $\text{H}_2$ like molecules and change the charge on both of the nuclei: $\text{Z}_2^{(2e)}$. Infinitely stretched $\text{Z}_2^{(2e)}$ binds two electrons, one on each nucleus with a total energy of $-2Z^2E_h$, for all values $Z > 0$. Let us now consider the opposite extreme with zero separation, the united atom, that is a single nucleus with charge $2Z$ that holds 2 electrons. For example, for two $Z=1$ protons (i.e. $\text{H}_2$) the corresponding united atom is a He atom, whereas for $Z=0.5$ protons a united atom of $\text{H}^-$ is obtained. Note that the second electron in He is bound by $-0.903E_h$ (the electron affinity of $\text{He}^+$) whereas the second electron in $\text{H}^-$ is only just bound, as the electron affinity of the H atom is now only $-0.028E_h$. Hence, if the nuclear charge on the protons is further reduced to 0.45, the united atom will have a charge of 0.9, such that now it is unable to bind two electrons. Therefore, at some point in between $\infty$ and 0, for $Z = 0.45$, the $\text{Z}_2^{(2e)}$ system undergoes a transition from being able to bind two electrons to only being able to bind 1 electron. This concept is illustrated in Fig. 4 which contains the binding curves of both $\text{Z}_2^{(1e)}$ and $\text{Z}_2^{(2e)}$ with a nuclear charge of 0.45 from FCI calculations in a large diffuse basis set. For large bond length the energy with two electrons is much lower than the energy with one electron. However, as the bond length is decreased the second electron becomes more weakly bound until at around 2 Å the molecule only binds one electron. This means a well characterized transition into metallic behavior for the two electron system such that the ionization energy is the same as the electron affinity, $I = A = 0$, and the unbound electron is released. This is one of the simplest illustrations of an insulator to metal transition, and it cannot be seen in $\text{H}_2$. Density functional approximations such as PBE completely fail to describe this behaviour as they have an incorrect $Z_2^{(1e)}$ curve (delocalization error[4]), an incorrect $Z_2^{(2e)}$ curve (static correlation error[20]) and an incorrect energetic preference for $\text{Z}_2$ with fractional numbers of electrons (the failure for the flat-plane[21]).

In conclusion, the foray into the theoretical world of fractionally charged nuclei allows us to directly visualize fundamental complexities of electronic structure in real space. The integer nature of electrons is critical in processes such as electron transfer or conductance and is seen in the $\text{HZ}^{(1e)}$ and $\text{HZ}^{(2e)}$ molecules. $\text{HZ}^{(1e)}$ shows the particle behavior of a single electron. This is not described by approximate methods such as DFT due to an inherent bias towards fractional electrons leading to a delocalization error that can be clearly seen in real space. It should be noted, however, that $\text{HZ}^{(1e)}$ does not capture the derivative discontinuity as it only has a single electron and, for example, $E_{xc} [\rho] = -J [\rho]$ (a smooth differentiable functional with no derivative discontinuity) is exact. A clear picture of the derivative discontinuity is given by the density of stretched $\text{HZ}^{(2e)}$. This shows the integer nature of two electrons that is very challenging to describe, for example, an orbital functional such as RHF completely fails. Electron hopping and a conical intersection can be seen in the chemical reaction of the $\text{HZH}^{(1e)}$ system. The essence of a metal-insulator transition is shown in the $\text{Z}_2^{(2e)}$ molecule for $Z = 0.45$. It undergoes a geometry dependent transition from binding two electrons to only binding one electron with a metallic electron unbound from the nuclei, characterized by $I = A = 0$. The physics encapsulated in the behavior of electrons in all these examples is at the heart of processes from electron transport to chemical reactions and the insulating to metallic transition in materials. It is only the use of fractional nuclei that reveals the full complexity of the electronic structure offering a massive challenge for approximate density and wave-function based methods.

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