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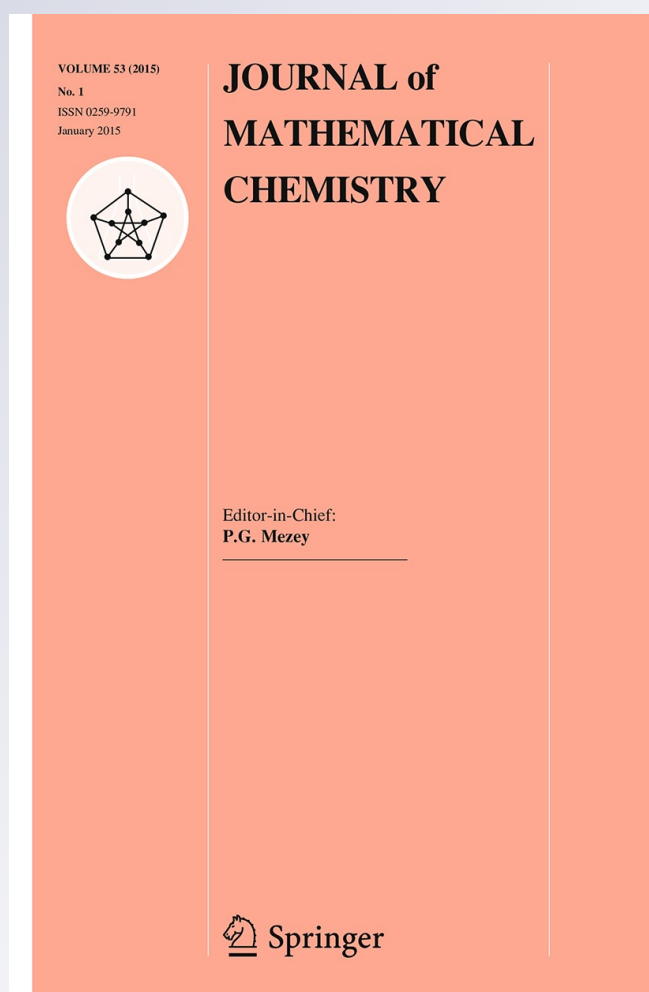
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Electronic densities in systems with fractionally charged nuclei: a symmetry breaking study

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Abstract This work reports an extension of the recent study on changes of electronic structures in systems possessing nuclei with fractional charges (Cohen and Mori-Sánchez in *J Chem Phys* 140:044110, 2014). Using the simple Hückel framework we show that the introduction of fractional charges in molecular systems causes a symmetry breaking which leads to strong changes in the electronic densities respect to their counterpart conventional systems with integer nuclear charges. Numerical determinations in simple one- and two-electron systems within this model are qualitatively compared with the results arising from the full configuration interaction method. The described procedure allows to study ground and excited states as well as the dissociation products when the bond lengths of the molecules are stretched.

Keywords Symmetry breaking · Hamiltonians with fractional nuclear charges · Electronic densities · Coordinate scaling

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1 Introduction

The formulation of electronic Hamiltonians to describe molecular systems whose nuclei possess electric charges quantified by rational numbers instead of integers has proved useful to tackle the study of interesting problems in quantum chemistry and molecular mechanics. It provides a more classical interpretation of some aspects of quantum chemistry removing the quantization of nuclear charges. The finite-size scaling applied to the Schrödinger equation, the molecular grand-canonical theory, the design of molecules for target properties, the understanding and error reduction in density functional calculations, etc, are paradigmatic examples of studies which involve fractional nuclear charges in the electronic Hamiltonians [1–16]. This extended formulation provides changes in the electronic external potential but it does not alter the nature of the Schrödinger equation of the molecular system and consequently any electronic description can be applied to this new approach. In Ref. [17] it has recently been reported that dramatic changes occur in the electron density of one- and two-electron molecules when the nuclear configuration is modified. Such remarkable effects appear when some nuclear charges are formulated by fractional numbers and the molecular geometry is greatly stretched. Some of those effects have been interpreted as transfer, hopping and removal of electrons by means of numerical determinations performed at configuration interaction (FCI) levels. However, these effects are not longer exhibited when other treatments are used for describing the system. In the case of the simple H_2^+ molecule, the symmetry breaking observed in the large dimensional limit has been suggested as a possible cause which might explain the appearance of these effects [17].

The main purpose of this report is to implement a further discussion and clarification of the changes in the electron density of such simple molecular systems. In order to achieve this purpose, we have formulated the Hamiltonian matrices within the Hückel model. The framework of this model turns out particularly suitable to analyze in a simple way the influence of the symmetry breaking caused by the presence of fractional nuclear charges. The results have been compared with those provided by the FCI method, showing that both procedures lead to similar qualitative predictions for the ground state and for the excited ones. This behavior guarantees the reliability of our proposal to predict dissociation products in stretched molecules. Another purpose of this work is to indicate that the presence of atomic nuclei with fractional charges in electronic Hamiltonians is a natural consequence when those operators are reformulated within scaling methods.

This work has been organized as follows. The second section describes the quantum-mechanical effects that can be ascribed to the symmetry breaking in the case of one-electron two- and three-center systems, by means of the well-known Hückel approximation. In the third section we perform a detailed analysis of energies, electronic densities and dissociation products in one- and two-electron systems, highlighting the role played by the fractional nuclear charges. The section four reports the relationship between the coordinate scaling and the fractional charges. Finally, in the last section we summarize the main conclusions of this work.

2 The symmetry breaking

We will refer to the one-electron linear molecules $\text{HZ}^{(1e)}$ and $\text{HZH}^{(1e)}$, where Z denotes the charge of one of the protons, which is allowed to be non-integer. In order to reduce the discussion to the symmetry aspects of these systems we resort to the well known Hückel approximation [18]. For example, for the molecule $\text{HZ}^{(1e)}$ we choose the Hamiltonian matrix

$$\mathbf{H}(\xi, b) = \begin{pmatrix} -1 & -b \\ -b & -1 + \xi \end{pmatrix} \quad (1)$$

where ξ accounts for the deviation from the integer charge on one of the atoms and $b \geq 0$. The eigenvalues e_i and eigenvectors \mathbf{v}_i of the symmetric case $\mathbf{H}(0, b)$ are given by

$$\begin{aligned} e_1 &= -1 - b, \quad \mathbf{v}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ e_2 &= -1 + b, \quad \mathbf{v}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \end{aligned} \quad (2)$$

for all values of b . This Hamiltonian is invariant with respect to the unitary transformation

$$\mathbf{U} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (3)$$

$\mathbf{UH}(0, b)\mathbf{U} = \mathbf{H}(0, b)$ ($\mathbf{U}^\dagger = \mathbf{U}^{-1} = \mathbf{U}$). It represents either the inversion operation i or a rotation C_2 of the $D_{\infty h}$ point group that one customarily chooses to describe the symmetry of a homonuclear diatomic molecule. Since the models discussed in this section are extremely simple, any of these two symmetry elements is sufficient for the description. The vectors (2) are also eigenvectors of \mathbf{U} and the symmetry is unbroken for all values of b including $b \rightarrow 0$, which in this oversimplified model is equivalent to internuclear distances $R_{\text{HZ}} \rightarrow \infty$.

On the other hand, the eigenvalues and eigenvectors of $\mathbf{H}(\xi, 0)$ are

$$\begin{aligned} e_1 &= -1, \quad \mathbf{w}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ e_2 &= -1 + \xi, \quad \mathbf{w}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{aligned} \quad (4)$$

These vectors are not longer eigenvectors of \mathbf{U} , meaning a symmetry breaking. We clearly appreciate that a slight change in ξ yields a dramatic change in the electron density when R_{HZ} is large enough (b small enough). For example, when $\xi > 0$ the ground state is given by \mathbf{w}_1 , whereas \mathbf{w}_2 is the eigenvector with the lowest eigenvalue when $\xi < 0$. When $\xi = 0$ the ground states approaches to \mathbf{v}_1 as $b \rightarrow 0$ as shown above. The three cases describe a diatomic molecule with its ground-state electron density distributed according to three quite different ways.

The Hückel model for the linear $\text{HZH}^{(1e)}$ molecule in a symmetric nuclear configuration is

$$\mathbf{H}(\xi, b) = \begin{pmatrix} -1 & -b & 0 \\ -b & -1 + \xi & -b \\ 0 & -b & -1 \end{pmatrix} \quad (5)$$

This Hamiltonian matrix is invariant with respect to the unitary transformation

$$\mathbf{U} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad (6)$$

$\mathbf{UH}(\xi, b)\mathbf{U} = \mathbf{H}(\xi, b)$ ($\mathbf{U}^\dagger = \mathbf{U}^{-1} = \mathbf{U}$). Its meaning is similar to the one discussed above.

The eigenvalues e_i and eigenvectors \mathbf{v}_i of $\mathbf{H}(0, b)$ are

$$\begin{aligned} e_1 &= -1 - \sqrt{2}b, \mathbf{v}_1 = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} \\ e_2 &= -1, \mathbf{v}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \\ e_3 &= -1 + \sqrt{2}b, \mathbf{v}_3 = \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} \end{aligned} \quad (7)$$

for all values of b . The vectors (7) are also eigenvectors of \mathbf{U} and the symmetry is unbroken for all b , including $b \rightarrow 0$.

The eigenvectors of $\mathbf{H}(\xi, b)$ retain their symmetry as $b \rightarrow 0$; therefore, the eigenvalues e_i and eigenvectors \mathbf{w}_i of $\mathbf{H}(\xi, b \rightarrow 0)$ are

$$\begin{aligned} e_1 &= -1, \mathbf{w}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \\ e_2 &= -1, \mathbf{w}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \\ e_3 &= -1 + \xi, \mathbf{w}_3 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \end{aligned} \quad (8)$$

for all values of ξ , except $\xi = 0$ that was separately discussed above. These vectors are also eigenvectors of \mathbf{U} and the symmetry is unbroken. In this case, when $b \rightarrow 0$ the ground state is given by \mathbf{w}_1 when $\xi > 0$ (because of symmetry conservation), by \mathbf{v}_1 when $\xi = 0$ and by \mathbf{w}_3 when $\xi < 0$. Once again we appreciate that small changes in ξ result in dramatic changes in the electron density when the side atoms are sufficiently far away.

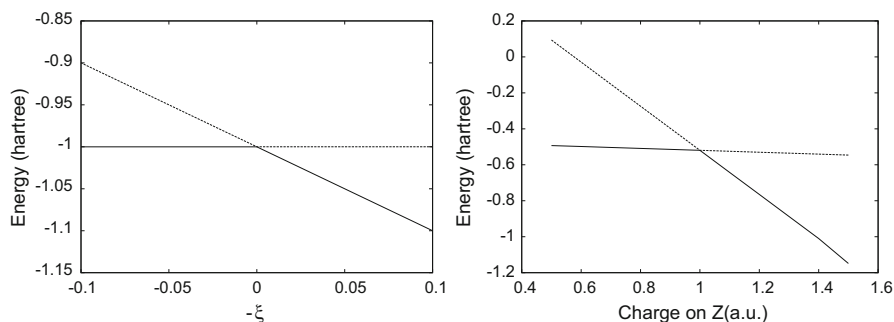


Fig. 1 Electronic energy of the two states of the $\text{HZ}^{(1e)}$ molecule versus ξ for the Hückel model (*left*) and versus Z for the actual system (*right*). $R_{\text{HZ}} = 8.5 \text{ \AA}$; basis set STO-3G

The conclusions drawn from this extremely simple model clearly reveal that symmetry breaking or symmetry conservation are inherent to the effects of fractional charges on the nuclei of the one-electron systems discussed in Ref. [17]. The Hückel model mentioned above also describes other properties of the actual molecular systems that we discuss in the following. In order to calculate the energy of the molecules we resorted to the FCI code calculations based on STO-3G orbitals available in Ref. [19]. Both the Hückel model and the FCI one with a minimal basis set produce only two states for $\text{HZ}^{(1e)}$ molecule and three states for the $\text{HZH}^{(1e)}$ one. For example, Fig. 1 shows the energy of the two electronic states of $\text{HZ}^{(1e)}$ versus ξ and versus Z for both the Hückel model and the actual system respectively, with $b = 0.01$ and $R_{\text{HZ}} = 8.5 \text{ \AA}$. Figure 2 shows the three levels of the $\text{HZH}^{(1e)}$ molecule calculated by both computational levels with $R_{\text{HZ}} = 8.5 \text{ \AA}$ and $b = 0.1$. In order to compare the electronic energies of the Hückel model with those of the actual system we arbitrarily choose $b = e^{-R_{\text{HZ}}}$. Figures 3 and 4 show results for both treatments, for different values of ξ and Z .

The analysis of the behavior of the electron density for two-electron systems requires a careful consideration of the energy of the fragments into which the molecule dissociates when bond lengths are stretched.

3 Energy analysis

The molecule $\text{HZ}^{(1e)}$ in the ground state dissociates into the fragments $\text{H}^- + \text{Z}^+$ or $\text{H}^+ + \text{Z}^-$ when $Z < 1$ or $Z > 1$, respectively. In other words, the dissociation process always leads to the fragments with lowest energy and the electron density is localized on H or Z, respectively. When $Z = 1$ there is identical probability of finding the electron on each nucleus. Such a localization also takes place when the internuclear distance R_{HZ} is sufficiently large as discussed in Ref. [17]. On the other hand, the first excited state yields fragments with higher energy and, therefore, its behavior is quite the opposite, namely the electron density will be localized on H or Z when $Z > 1$ or $Z < 1$, respectively.

In the study of the linear $\text{HHH}^{(1e)}$ molecule, we assume that the distance between the side nuclei is sufficiently large (say 10 \AA). If the central nucleus is slightly displaced

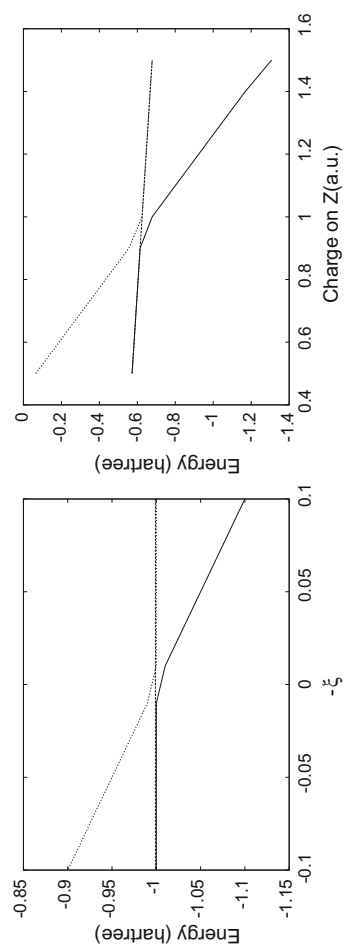


Fig. 2 Electronic energy of the three states of the $\text{HZH}^{(1e)}$ linear molecule versus ξ for the Hückel model (*left*) and versus Z for the actual system (*right*). $R_{\text{HZ}} = 8.5 \text{ \AA}$; basis set STO-3G

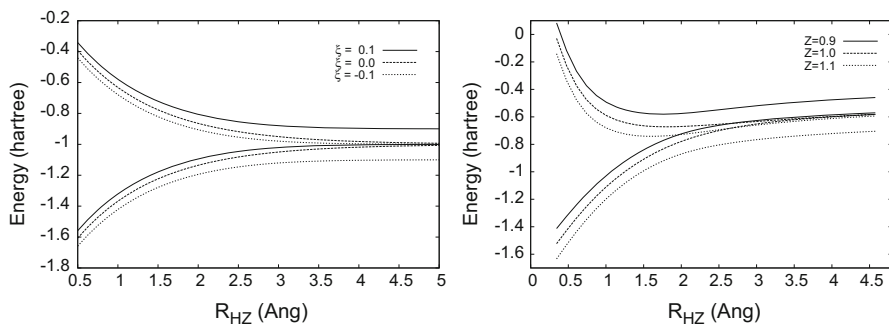


Fig. 3 Electronic energy of the two states of the $HZ^{(1e)}$ molecule versus R_{HZ} for the Hückel model (*left*) and the actual system (*right*). Basis set STO-3G

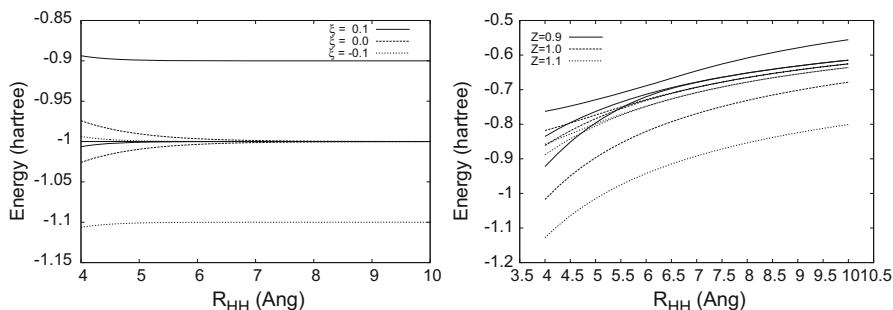


Fig. 4 Electronic energy of the three states of the $HZH^{(1e)}$ linear molecule versus R_{HH} for the Hückel model (*left*) and the actual system (*right*). Basis set STO-3G

to the left of the center of the nuclear configuration we can view the system as a diatom $HZ^{(1e)}$ with an effective charge $Z > 1$ due to the perturbation by the positive charge of the rightmost nucleus in the three-center molecule. It then follows from the above discussion for the diatomic molecule that the electron density will be localized on the central nucleus. Likewise, if the middle nucleus is slightly displaced to the right of the center of the nuclear configuration we can apply the same above mentioned reasoning for a diatomic molecule $ZH^{(1e)}$ with $Z > 1$. The electron density will again be localized on the central nucleus. If that central nucleus is exactly in the middle then the electron density is also expected to be localized on the central nucleus. We have carried out a FCI calculation with a minimal basis set of STO-3G atomic orbitals and their results have been collected in Fig. 5. As can be observed, these results confirms what we have just discussed.

The linear $HZH^{(1e)}$ system with $Z = 1.1$ and a large distance between the leftmost and rightmost nuclei has also been studied within this methodology. In this case we expect the electron density to be localized on the central atom when it is at the middle or slightly to the left or right of the nuclear configuration. This simple argument is corroborated by the results reported in Fig. 6.

Let us now suppose that $Z = 0.9$ and the middle nucleus is slightly to the left of the center of the nuclear configuration. Since the rightmost nucleus is quite far away, its

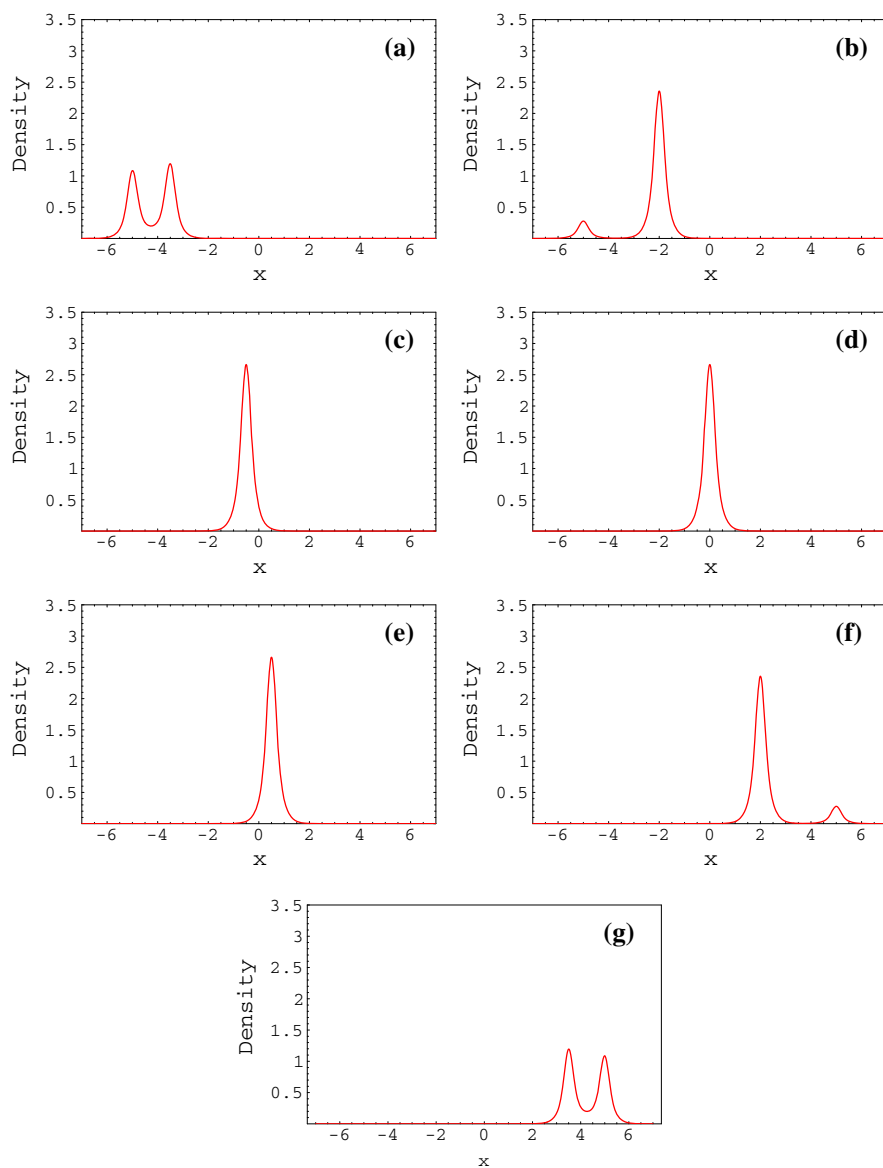


Fig. 5 Electron density for the linear molecule $\text{HHH}^{(1e)}$. The left and right atoms are clamped at $R_1 = -5 \text{ \AA}$ and $R_3 = 5 \text{ \AA}$, respectively, while the central one is located at $R_2 = x = -3.5 \text{ \AA}$ (a), -2.0 \AA (b), -0.5 \AA (c), 0.0 \AA (d), 0.5 \AA (e), 2.0 \AA (f) and 3.5 \AA (g)

effect on the middle nucleus is insufficient to overcome the 10 % difference between the nuclear charges of the HZ fragment. According to the above analysis for the diatom we conclude that the electron density will be localized on the leftmost atom. If the middle atom is slightly to the right of the center then we can think of the system as a diatom ZH with $Z < 1$. Obviously, in this case the electron density will be localized on the

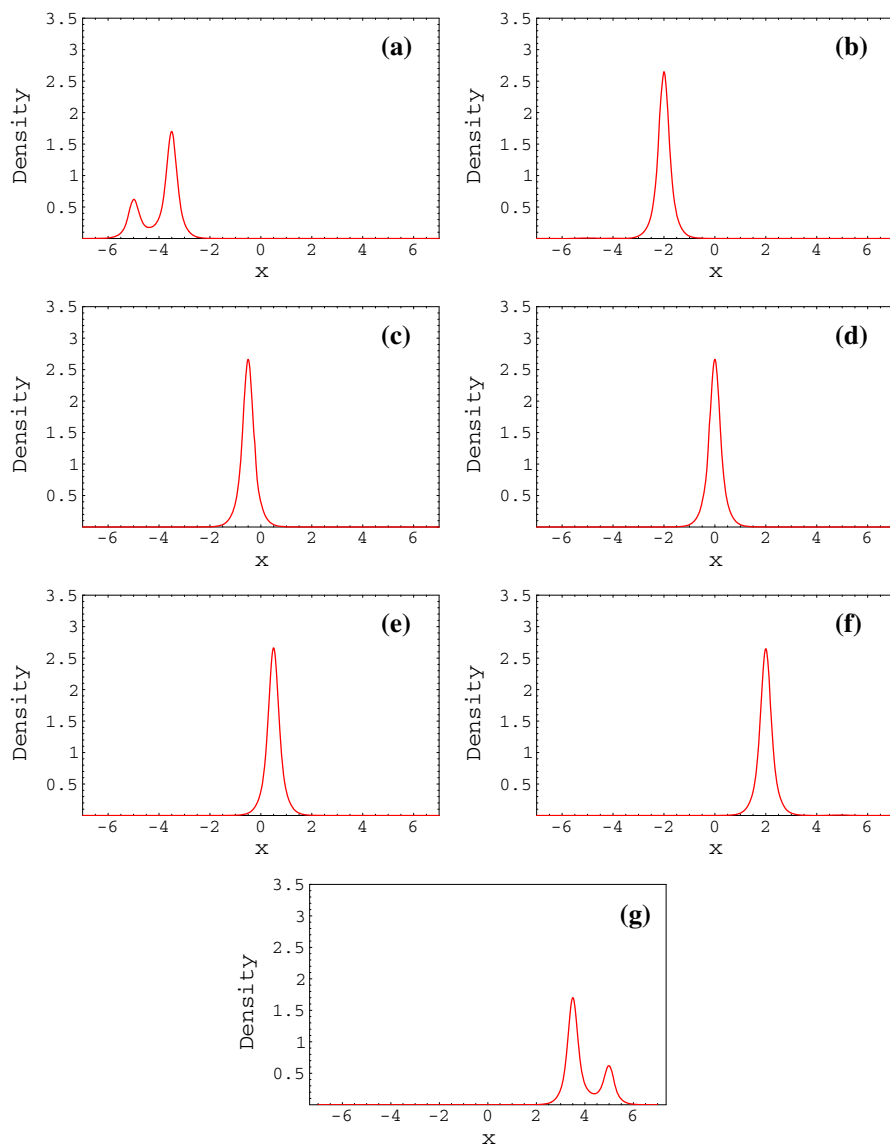


Fig. 6 Electron density for the molecule $\text{HZH}^{(1e)}$, $Z = 1.1$. The left and right atoms are clamped at $R_1 = -5 \text{ \AA}$ and $R_3 = 5 \text{ \AA}$, respectively, while the central one is located at $R_2 = x = -3.5 \text{ \AA}$ (a), -2.0 \AA (b), -0.5 \AA (c), 0.0 \AA (d), 0.5 \AA (e), 2.0 \AA (f) and 3.5 \AA (g)

rightmost atom. We can view the whole process just described as an electron hopping [17]. It is interesting to consider the symmetric nuclear configuration that has not yet been explicitly discussed. Since the electronic ground state is symmetrical we expect two electronic density maxima on the side nuclei because we can view the three-center molecule as a diatom HZ or ZH on the left or right, respectively. The effect of the remaining nucleus is insufficient to overcome the 10% difference between the charges

of the Z and H nuclei. However, the results shown in Fig. 7 are at variance with what we have just mentioned. It shows that when the middle nucleus is exactly at the center of the nuclear configuration the ground (d.1) and first-excited (d.2) states exhibit the electron densities located on the right and left nuclei, respectively. Such an unexpected outcome is due to numerical errors that strongly affect the results because those states are almost degenerate. Therefore, the calculation process accidentally combines the symmetric and antisymmetric wave functions and produces those localized electron densities. This result clearly shows that in such cases it is judicious to impose the correct symmetry on the basis set (which we obviously did not do). Some time ago Davidson and Border [20] cautioned the researchers to properly take into consideration the molecular symmetry in order to avoid completely wrong results. The present FCI calculation is an example of it in the case of an extremely simple molecular system. In this case the numerical errors produce a symmetry breaking and the electronic wave function is no longer eigenfunction of the symmetry operators i and C_2 . If we move the side nuclei sufficiently to the center, keeping the molecule symmetric, the gap between the almost degenerate energy levels increases and the numerical errors do not break the symmetry as shown in Fig. 8. We appreciate that the subfigure (d) now exhibits the correct symmetry of the electron density for the symmetric nuclear configuration; that is to say, the electronic wave function is eigenfunction of i and C_2 . Figure 8 shows an interesting missing step in the electron-hopping process discussed in Ref. [17].

Let us now consider the first excited state of the linear $HHH^{(1e)}$ molecule when the side atoms are quite far apart. If the middle nucleus is slightly displaced to the left we can view this molecule as an $HZ^{(1e)}$ diatom with $Z > 1$. It follows from the above given argument for the diatom that the electron density will be localized on the leftmost H nucleus. If the middle nucleus is slightly displaced to the right then we have a $ZH^{(1e)}$ diatom with the electron density on the rightmost H nucleus because $Z > 1$ as above argued. We appreciate that there is an electron hopping from the leftmost nucleus to the rightmost one even when there are no fractional nuclear charges.

In the case of two-electron systems the analysis is slightly more complicated. Let us consider the molecule $HZ^{(2e)}$ in the ground state that can dissociate along the following three channels, $H^- + Z^+$, $H + Z$, or $H^+ + Z^-$ with energies $E_{He}(1)$, $-1/2 - Z^2/2$ or $E_{He}(Z)$, respectively, where $E_{He}(Z)$ is the energy of an Helium-like atom with nuclear charge Z . We define two critical charges Z_c and Z'_c given by $E_{He}(Z_c) = -1/2 - Z_c^2/2$ and $E_{He}(Z'_c) = -Z_c'^2/2$. If $Z_c < Z$ the molecule dissociates into $H^+ + Z^-$, if $Z'_c < Z < Z_c$ it dissociates into $H + Z$ and if $Z < Z'_c < Z_c$ it dissociates into $H^- + Z^+$ leading to different electron densities for the diatomic molecule when the internuclear distance is sufficiently large. The perturbation expansion for $E_{He}(Z)$ calculated by Montgomery [21] is useful to estimate both Z'_c and Z_c with sufficient accuracy. Present results $Z'_c \approx 0.912$ and $Z_c \approx 1.666340041$ agree perfectly well with those estimated in Ref. [17] by means of the simple Mulliken atomic population analysis.

4 Fractional charges from coordinate scaling

In this section we show that it is possible to obtain the electronic energy and electron density for a one-electron system with fractional charges starting from the same prob-

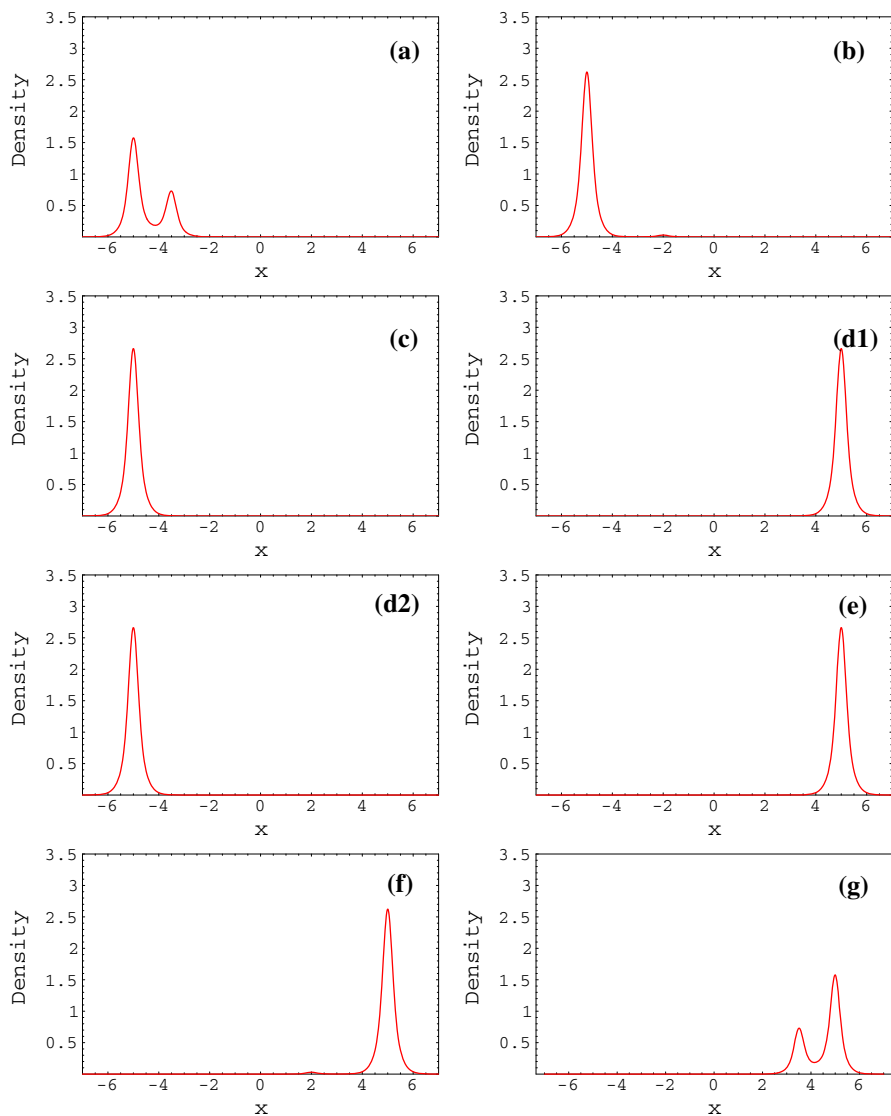


Fig. 7 Electron density for the molecule $\text{HZH}^{(1e)}$, $Z = 0.9$. The left and right atoms are clamped at $R_1 = -5 \text{ \AA}$ and $R_3 = 5 \text{ \AA}$, respectively, while the central one is located at $R_2 = x = -3.5 \text{ \AA}$ (a), -2.0 \AA (b), -0.5 \AA (c), 0.0 \AA (d.1 for the ground state), 0.0 \AA (d.2 for the first-excited state), 0.5 \AA (e), 2.0 \AA (f) and 3.5 \AA (g)

lem with integer charges. As an example, consider the electronic Hamiltonian for the three-center problem

$$\hat{H}_e = -\frac{1}{2}\nabla^2 - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} - \frac{Z_3}{r_3}, \tag{9}$$

where $r_i = |\mathbf{r} - \mathbf{R}_i|$ is the distance from the electron to the nucleus i clamped at \mathbf{R}_i . All the expressions in this section can be straightforwardly generalized to any number

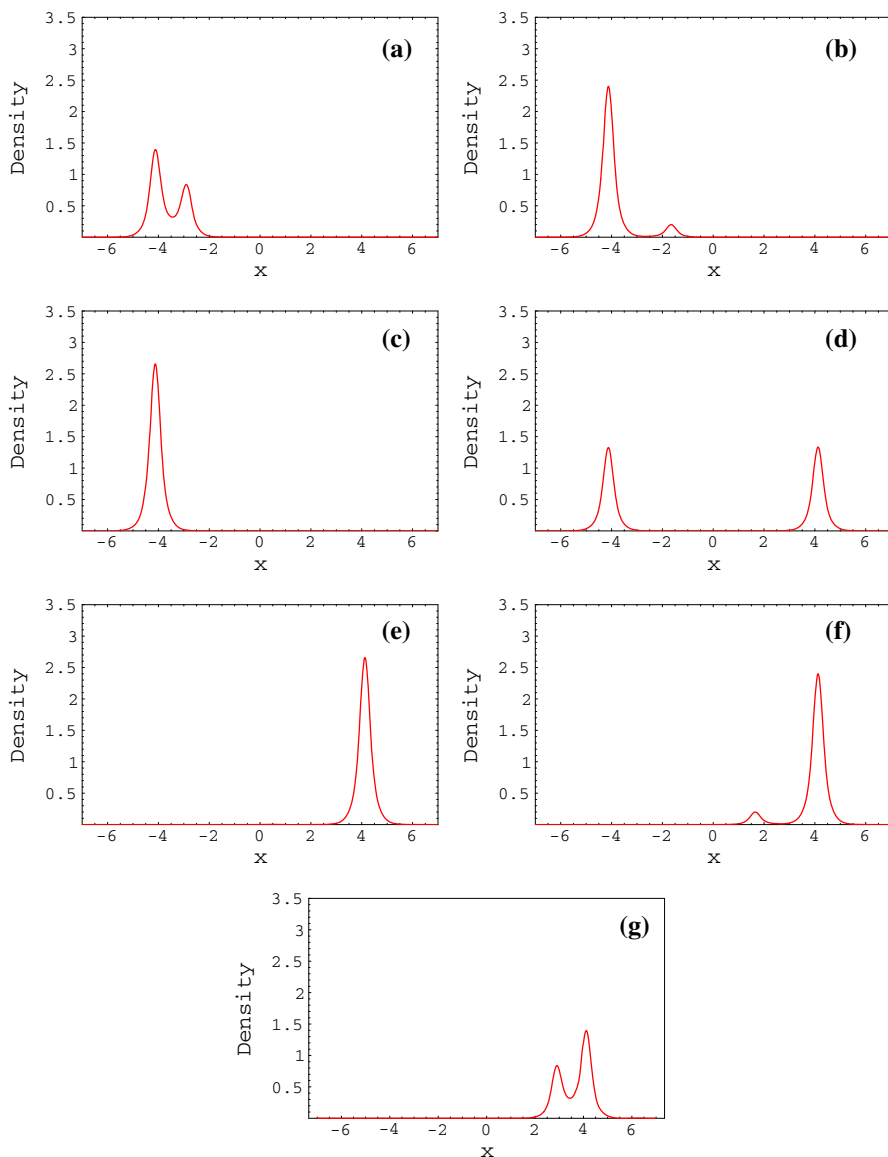


Fig. 8 Electron density for the molecule $\text{HZH}^{(1e)}$, $Z = 0.9$. The left and right atoms are clamped at $R_1 = -4.125 \text{ \AA}$ and $R_3 = 4.125 \text{ \AA}$, respectively, while the central one is located at $R_2 = x = -3.5 \text{ \AA}$ (a), -2.0 \AA (b), -0.5 \AA (c), 0.0 \AA (d), 0.5 \AA (e), 2.0 \AA (f) and 3.5 \AA (g)

of nuclei. This three-center problem is sufficient for the present purposes because if we choose $Z_3 = 0$ we obtain the two-center one already discussed above. In what follows we consider the case $Z_3 = Z_1$. The coordinate scaling

$$\mathbf{r} = L\mathbf{r}', \nabla^2 = L^{-2}\nabla'^2, \mathbf{R}_i = L\mathbf{R}'_i, r'_i = |\mathbf{r}' - \mathbf{R}'_i|, \quad (10)$$

leads to

$$L^2 \hat{H}_e = -\frac{1}{2} \nabla^2 - \frac{LZ_1}{r'_1} - \frac{LZ_2}{r'_2} - \frac{LZ_3}{r'_3}. \quad (11)$$

If we choose $L = 1/Z$ we have

$$Z^{-2} \hat{H}_e = -\frac{1}{2} \nabla^2 - \frac{Z_1/Z}{r'_1} - \frac{Z_2/Z}{r'_2} - \frac{Z_3/Z}{r'_3}. \quad (12)$$

If ψ_e is an eigenfunction of \hat{H}_e with eigenvalue E_e

$$\hat{H}_e \psi_e = E_e \psi_e \quad (13)$$

then Eq. (12) tells us that

$$Z^{-2} E_e(Z_1, Z_2, Z_3, \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = E_e(Z_1/Z, Z_2/Z, Z_3/Z, Z\mathbf{R}_1, Z\mathbf{R}_2, Z\mathbf{R}_3). \quad (14)$$

Obviously, from the calculation of $E_e(Z_1, Z_2, Z_3, \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ with integer charges we can obtain $E_e(Z_1/Z, Z_2/Z, Z_3/Z, Z\mathbf{R}_1, Z\mathbf{R}_2, Z\mathbf{R}_3)$ with fractional ones, which can be extended to electronic densities.

5 Concluding remarks

In this work, we have explained the nature of the strong changes in the electronic density undergone by a system when fractional nuclear charges are introduced in its electronic Hamiltonian. The simple Hückel model constitutes a suitable tool to show that the symmetry breaking caused by the utilization of nuclei with fractional charges is the origin of those effects. This conclusion is supported by the numerical determinations performed within the Hückel framework which qualitatively turn out to be similar to those arising from the exact FCI method. This methodology can be applied to the description of any electronic state providing the prediction of its dissociation products. Furthermore, we indicate that the formulation of electronic Hamiltonians with atomic nuclei with fractional charges can be applied to any system. We are currently working in our laboratories on other applications of this formulation.

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