Core-valence stockholder AIM analysis and its connection to nonadiabatic effects in small molecules

Paulo H. R. Amaral and José R. Mohallem^{a)}

Laboratório de Átomos e Moléculas Especiais, Departamento de Física, ICEx, Universidade Federal de Minas Gerais, Av. Antonio Carlos 6627, Belo Horizonte, Minas Gerais, Brazil

(Received 31 January 2017; accepted 1 May 2017; published online 17 May 2017)

A previous theory of separation of motions of core and valence fractions of electrons in a molecule [J. R. Mohallem *et al.*, Chem. Phys. Lett. **501**, 575 (2011)] is invoked as basis for the useful concept of Atoms-in-Molecules (AIM) in the stockholder scheme. The output is a new tool for the analysis of the chemical bond that identifies core and valence electron density fractions (core-valence stockholder AIM (CVSAIM)). One-electron effective potentials for each atom are developed, which allow the identification of the parts of the AIM which move along with the nuclei (cores). This procedure results in a general method for obtaining effective masses that yields accurate non-adiabatic corrections to vibrational energies, necessary to attain cm^{-1} accuracy in molecular spectroscopy. The clear-cut determination of the core masses is exemplified for either homonuclear (H_2^+ , H_2) or heteronuclear (HeH^+ , LiH) molecules. The connection of CVSAIM with independent physically meaningful quantities can resume the question of whether they are observable or not. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983394>]

I. INTRODUCTION AND REASONING

The interest in the description of the properties of a molecule in terms of its constituent atoms, with an emphasis on atomic charges, is kept alive in chemistry, despite no rigorous quantum chemical basis has been found for this procedure so far. Atoms-in-Molecules (AIM) are conceptual constructions, defined by *ad hoc* partitions of the molecular density, designed with this aim in view. AIM are thus considered as being not observables. The partition of the molecular density with boundary surfaces as in the models of Politzer and Harris¹ and Bader (QTAIM (Quantum Theory of Atoms in Molecules))² defines topological AIM, having mutually exclusive densities. These constructs yield non-spherical, non-superposing atoms.

On the other hand, the stockholder model proposed by Hirshfeld³ attempts to define AIM that mimic the atomic densities in the promolecule, namely, the sum of the atomic densities previous to deformation caused by chemical bonding. Stockholder AIM (SAIM from now on) then yield superposing and non-superposing density fractions. In applications to heteronuclear molecules, however, the original recipe for the density partition is not constrained to be the *best* partition. In practice, for strongly polar molecules, the original SAIM approach yields too lower atomic charges than their usually recognized values. It took some decades for SAIM to regain the attention of researchers, thanks to the development of new iterative algorithms.^{4–6}

In order to find a constraining procedure (somewhat analogous to the variational method for approximate wavefunctions) to define the best SAIM for heteronuclear molecules,

researchers resorted to the minimization of the information entropy.⁷ The Hir-I method of Bultinck *et al.*⁴ and the ISA (Iterative Stockholder Atoms) method of Lillestolen and Wheatley⁶ aim to iteratively reproduce SAIM in a molecule obeying this principle and corrected the original approach (called Hir), at least in the sense of generating atomic charges compatible with those reported in the literature. Details of the two approaches may be found in the cited articles. In consequence, SAIM are becoming popular in the analysis of chemical bonding.^{8–10}

Besides being helpful constructions in the practical sense, SAIM have also been a subject of intense debate, recently reviewed by Shahbazian,¹¹ concerning their physical meaning. The main criticism towards considering them as real physical objects seems to be based on that their connected properties, e.g., atomic charges, are neither measurable nor conceptually independent.^{7,12} The discussion would be enriched, on the other hand, in the event of the identification of independent properties of clear physical meaning, whose values could be directly connected to SAIM. Since real atoms are always in motion, in order to connect SAIM with physical quantities, it seems more reasonable to look for spectroscopic molecular properties, instead of just properties of the static electronic density at a rather idealized equilibrium geometry.

In this paper, we propose that the SAIM can have their physical embasement on a previous theory of the separation of movements of core and valence electrons (defined just below).¹³ Exploring effective atomic potentials, a core-valence-SAIM (CVSAIM) density partition is introduced. Upon identifying the CVSAIM core fractions, we connect them to non-adiabatic corrections to vibrational energy levels of small molecules, which are needed to reach the spectroscopy

^{a)} Author to whom correspondence should be addressed. Electronic mail: rachid@fisica.ufmg.br

accuracy of cm^{-1} . The approach is consistently applied to small molecules for which very accurate calculated non-adiabatic corrections are available, namely, H_2^+ , H_2 , and HeH^+ . For LiH , the comparison is performed directly with experimental vibrational energies, as well as with other calculations. As an important by-product, the CVSAIM analysis reveals more details of the chemical bonding than the standard AIM approaches, including SAIM itself.

The SAIM can be rationalized from the core-valence separation of motions, following their original definition from the one-electron molecular density ρ_{mol} . In a diatomic molecule AB , for example, being ρ_A^0 and ρ_B^0 the densities of the isolated atoms and $\rho_{mol}^0 = \rho_A^0 + \rho_B^0$ the density of the promolecule, the density of the SAIM corresponding to the bonded atom A is given by

$$\rho_A = w_A \rho_{mol} = \frac{\rho_A^0}{\rho_{mol}^0} \rho_{mol}, \quad (1)$$

with an analogous definition for ρ_B , where $w_A = \frac{\rho_A^0}{\rho_{mol}^0}$ plays the role of a statistical weight. It follows immediately that

$$\rho_{mol} = \rho_A + \rho_B, \quad (2)$$

as expected in any AIM theory. The SAIM densities superpose each other, since they spread over the entire coordinate space as an atomic density must do. This feature becomes fundamental as one tries to connect AIM to observable quantities, different from topological atoms.

In isolated electronic states, non-adiabatic effects on the energy levels are a consequence of fractions of electrons being dragged by the nuclei mainly as they vibrate. We refer to the nuclei plus the electrons attached to them during vibrations as *cores*. The fraction that lies between the atoms and moves slower during vibrations is called *valence*. In a recent paper,¹³ the quasi-adiabatic separation of motions of atomic cores and valence electron fractions was performed. A result from this work, which is important to the present context, is that the usual nuclear reduced mass that appears in the vibrational equation is replaced by a R -dependent reduced mass $\mu(R)$ of the cores, where $R \equiv R_{AB}$ stands for the internuclear separation.

Another point concerning the cited separation of motions deserves a more detailed explanation. The valence fraction of electrons is shared by the two atoms, being under the influence of both nuclei. The coulombic nuclear attraction over them is cancelled in average but the exchange effects still couple their motion, so that the populations of these fractions change as the molecule vibrates. All of this is very well known in quantum chemistry. What has been ignored for a long time is that, as a consequence, the fraction of valence electrons follows the nuclear movement much more slowly than the core fraction. This behavior implies that the molecular density can, to a good approximation, be divided into core and valence parts,

$$\rho_{mol} = \rho_{co} + \rho_{val}. \quad (3)$$

In order for Eqs. (2) and (3) to be consistent, we must assert to each SAIM a valence part, so that

$$\rho_{mol} = \rho_{A,co} + \rho_{A,val} + \rho_{B,co} + \rho_{B,val}. \quad (4)$$

Of course, despite its consistency with the theory of core-valence separation, the previous argument does not prove that the so-defined AIM are *real* AIM. In fact, other partition schemes could eventually be devised, also reproducing Eq. (2). It remains to be checked whether the ρ_{co} and ρ_{va} obtained from the CVSAIM scheme bring new insights on chemical bonding and/or are connected to measurable quantities. These fundamental points are addressed in Sections II–IV.

II. EFFECTIVE POTENTIALS FOR SAIM AND CORE MASSES

Once the molecular density $\rho(\vec{r})$ is available, the first step of our calculations involves obtaining its SAIM partition. For this, two main approaches appeared in the literature, which are outlined as follows.

In the Hir-I procedure,⁴ the molecular density is partitioned in SAIM densities according to Eqs. (1) and (2). The densities of the isolated atoms ρ_A^0 and ρ_B^0 are initially used to start the iterative procedure. The SAIM densities obtained in the first iteration have fractionary populations. New isolated SAIM densities ρ_A^1 and ρ_B^1 are then obtained from these populations, by using Fukui functions, built in order to describe the change of the electron density under a change in the number of electrons.¹⁴ For symmetric configurations of homonuclear molecules, just the first step leading to ρ_A^1 and ρ_B^1 is enough (Hir). In other cases, some further iterations are needed to converge the SAIM (Hir-I). The ISA procedure⁶ differs from Hir-I by just replacing the Fukui procedure by spherical averaging of the SAIM from the previous iteration. Like the Hir-I procedure, a single iteration is needed for symmetric homonuclear systems, while with few iterations the convergence is achieved for heteronuclear molecules. The converged SAIM then obeys

$$\rho_A = \frac{\rho_A^{n-1}}{\rho_{mol}^{n-1}} \rho_{mol}, \quad (5)$$

within a convergence criterion. The two approaches, compared in Ref. 15 for usual applications, have been tested in this work. They show almost equivalent performances, except for HeH^+ , since the Fukui function does not apply properly to an H atom with less than one electron. So, for the sake of consistency, we display only the ISA results for all the systems studied.

In the cases of well isolated ground electronic states, non-adiabatic corrections to vibrational energy levels have been evaluated with high accuracy by taking the difference of the energies calculated with nuclear masses, from those obtained with empirical effective masses^{16,17} in the vibrational equation. In previous calculations in our group, the R -dependent effective masses, now identified as core masses,¹³ are tried case by case, following heuristic arguments. Diagonal Mulliken populations were used for the evaluation of core masses for H_2^+ , H_2 ,¹⁸ H_3^+ ,¹⁹ and isotopologues. Application to LiH as well as improvement of the results for H_2 was possible by extracting the core masses from the coefficients of suitably chosen valence-bond structures.²⁰ However, these wavefunction-dependent applications suffer from the lack of a common approach. For example, the recipes for core masses from VB Ansätze that worked for LiH

and H_2 are not consistent between themselves, meaning that the basis for these successful applications is not yet fully understood.

It seems mandatory that a universal approach be based not on trial wavefunctions, but on wavefunction-independent accurate molecular densities. The problem with such an approach is how to distinguish the core and the valence parts of each SAIM from the full molecular density. A hint to this problem comes from homonuclear systems, H_2 , for example, see the top of Figure 1. From symmetry, it seems reasonable to take the nonsuperposed parts as the cores, one of them shadowed in Figure 1, taking the rest as valence. However, this easy procedure does not work in the heteronuclear cases, since the range of the atomic potentials is no longer equivalent and symmetry is no help anymore.

In order to overcome this problem, giving also physical support to the procedure for homonuclear molecules, we devise a general approach for obtaining the effective core densities from the SAIM partition of the molecular density. For this, we first construct effective one-electron potentials for each atom, from the molecular density, by the following elementary procedure. Starting from each atomic center ($r = 0$), say A , a charge $q(r_A)$ is obtained by numerical integration,

$$q(r_A) = 4\pi \int_0^{r_A} \rho_{mol} r^2 dr. \quad (6)$$

The effective potential $V_A(r_A)$ is simply

$$V_A(r_A) = -\frac{Z_A - q(r_A)}{r_A}, \quad (7)$$

where Z_A is the charge of nucleus A , r_A ranges from 0 to a limit value set by the condition $V_A(r_A) = 0$, and the same procedure is followed for atom B . Since $q(r)$ is taken from ρ_{mol} instead from the corresponding SAIM density, $V(r)$ goes to zero at finite distances, see Figures 1, 4, and 6.

Now, consider the molecular density already partitioned in SAIM components. On physical grounds, the core fraction

of the electron density of SAIM A , $\rho_{A,c}$, is chosen as the part of the SAIM density preponderantly subject to the potential V_A , that is, corresponding to the region where V_A is more attractive than V_B . The bottom parts of Figures 1, 4, and 6 in Section III illustrate these ideas in more detail, for H_2 , HeH^+ , and LiH , respectively. It can be seen that a part of the density of each SAIM falls outside the so-defined core region and accounts together for the valence density ρ_{va} , that is, the electron fraction that moves slowly as the nuclei vibrate. For homonuclear molecules (Figure 1), it coincides with the SAIM superposed parts, as seen before. See, in Figures 4 and 6, that the different core-valence partitions of each SAIM depend on the relative ranges of the potentials.

In view of its new features, from now on we use CVSAIM to refer to the present method. We keep using SAIM to refer to the stockholder AIM.

III. NON-ADIABATIC CORRECTIONS

The electronic mass which is to be added to the nuclear one to compose the core mass is obtained by the numerical volume integration of the core part of the SAIM density, so that the effective mass of nucleus A is

$$m_A(R) = m_A^{nuc} + m_e \int \rho_{A,c}(\vec{r}, R) d\vec{r}^3, \quad (8)$$

where m_A^{nuc} is the mass of the bare nucleus A and m_e is the electron mass, with an analogous expression for $m_B(R)$. Once this procedure is accomplished for a grid of R , the effective reduced mass of the cores is calculated as

$$\mu(R) = \frac{m_A m_B}{m_A + m_B}. \quad (9)$$

Vibrational energies, including non-adiabatic corrections, are obtained by solving the vibrational equation with the effective reduced mass [Eq. (9)]. Either an algorithm that allows R -dependent reduced masses²¹ or common algorithms running with a constant reduced mass can be used, provided that, in the second case, the masses are averaged over the vibrational states^{13,18} as

$$\langle m_{A,v}^{i+1} \rangle = \int m_A^i(R) [\chi_v^i(R)]^2 dR, \quad (10)$$

where $\chi_v^i(R)$ is the wavefunction for the vibrational level v at iteration i . As a general rule, constant averaged masses work well for homonuclear molecules, while for the heteronuclear ones the R -dependent masses work better. This rule is followed in the next applications. For comparison with other calculations, recall that the energies obtained with the use of Eq. (9) minus those obtained with the nuclear masses are the non-adiabatic corrections. These corrections amount to some units of cm^{-1} . For them to be meaningful, the energy levels must be obtained by solving the vibrational equation with a potential energy curve (PEC) having appropriate accuracy, which implies not only a high accurate Born-Oppenheimer electronic calculation but also the inclusion of diagonal corrections (usually referred to as diagonal-Born-Oppenheimer-corrections, DBOCs) and possibly relativistic corrections.

We perform applications to the apolar covalent H_2^+ and H_2 , the polar weakly covalent (or van der Waals) HeH^+ , and

FIG. 1. Cut along the molecular axis z of the total and CVSAIM densities and effective potentials for H_2 at equilibrium geometry. The shaded areas correspond to the electron fractions that follow the nuclear vibrations (cores). The vertical dashed line is a boundary between the core and valence parts of each CVSAIM.

the polar ionic-covalent LiH molecules. The aim is to investigate the central hypothesis of this work, namely, an actual spectroscopic role of SAIM, for different fundamental bonding schemes. Furthermore, for these four small molecules, it is possible to perform a comparison with *ab initio* non-adiabatic calculations and even with measurements (LiH) of vibrational transitions having spectroscopic (cm^{-1}) accuracy, where the non-adiabatic corrections play a fundamental role.

Densities are obtained by running the Gamess package²² on the full-CI level for H_2 and HeH^+ and on the CISD (single and double excitations) level for LiH.

A. H_2^+ and H_2

As already discussed, calculations are much simpler for homonuclear molecules in symmetric configurations (all configurations of homonuclear diatoms), since the electronic density must be equally divided between the SAIM. The Hir approach already gives the best partition. The electronic densities of the two molecules were obtained with the aug-cc-pV5Z basis set. Figure 1 shows the total and the SAIM densities for H_2 at the equilibrium distance $R_{eq} = 1.40$ a.u. Each core (shadowed just for one SAIM) is identified as the part of the SAIM density preponderantly subject to the corresponding potential. They are separated from the valence part, in the figure, by a vertical hatched line. Results for H_2^+ refer to $R_{eq} = 2.00$ a.u.

Just a single iteration is needed to converge the vibrational masses in Eq. (10). The effective averaged reduced mass and the corresponding non-adiabatic corrections were obtained as described in Sec. II. The PECs for the vibrational equation, including DBOCs, are the same used in a previous work.¹⁸ Figures 2 and 3 show remarkable agreement between the non-adiabatic corrections evaluated here and the most accurate *ab initio* calculations. For comparison, atomic mass results (meaning half electron for each atom in H_2^+ and one electron each for H_2) are also included, yielding the worst results. Curiously, between the two sets of *ab initio* H_2 calculations in Figure 3 by Wolniewicz,^{23,24} the present results agree better with the 1983²³ results than with the more recent 1995²⁴ ones,

FIG. 2. Nonadiabatic corrections (cm^{-1}) to the vibrational levels of H_2^+ , *a*,³⁶ and *b*.³⁷

FIG. 3. Nonadiabatic corrections (cm^{-1}) to the vibrational levels of H_2 , *a*,³⁸ *b*,²³ and *c*.²⁴

which are improved in energy. At this point, we are unable to explain this finding.

B. HeH^+

Applications to heteronuclear molecules demand the iterative ISA procedure, as discussed previously. The two-electron molecular ion HeH^+ differs from H_2 for its heteronuclear character. Its molecular density was also calculated with the aug-cc-pV5Z basis set. To the best of our knowledge, there is no evaluation of atomic charges for HeH^+ other than doubtful Mulliken charges. However, based on a further accurate calculation,²⁵ Tung *et al.* argued that, in low vibrational states, 0.16 a.u. of electron mass moves with H and 0.84 a.u. with He (there is no consideration of a valence charge in that approach). Figure 4 shows a cut of the CVSAIM partition of the density, the potentials, and the corresponding ranges that define the SAIM, which are now different for each nucleus, as expected. At the equilibrium distance $R_{eq} = 1.46$ a.u., we obtain electronic charges of +0.256 a.u. for the He SAIM and +0.744 a.u. for the H^+ SAIM. After core-valence separation,

FIG. 4. Cut along the molecular axis z of the total and CVSAIM densities and effective potentials for HeH^+ at equilibrium geometry. The shaded areas correspond to the electron fractions that follow the nuclear vibrations (cores). The vertical dashed line is a boundary between the core and valence parts of each CVSAIM.

the core masses result in 1.595 and 0.199 a.u., so that the valence fractions are 0.149 and 0.057 a.u., respectively. The full valence fraction is then quantified as 0.206 a.u. The He SAIM donates charge to the H^+ SAIM core and keeps almost all valence fractions on its SAIM. A small part of the valence fraction belongs to the H^+ SAIM. Once we agree that the share of the valence fraction by the two atoms characterizes a covalent bond, from the CVSAIM point of view, the bond in HeH^+ appears to be really slightly covalent, despite the He SAIM retains much of its noble character, that is, 1.74 of 2.0 electrons still belong to the He SAIM. A future systematic study of bonding characterization by the present method can introduce further insights on the subject.

Having the R -depending effective nuclear masses, the core reduced mass $\mu(R)$ is obtained from Eq. (8) and, as argued before, the nuclear equation with variable reduced mass is solved in this case. The HeH^+ PEC from a full-correlated method including DBOCs is taken from Ref. 26. The resulting non-adiabatic corrections, shown in Figure 5, agree very well with those from the same work. Since Tung *et al.*²⁵ reported the mass values for low vibrational states, we believe the agreement is good and notice a consistent evaluation of charges and non-adiabatic corrections from the CVSAIM partition. Again, atomic masses (meaning here two electrons for He and no electron fraction for H^+) yield bad corrections.

C. LiH

LiH is a singular case, in view of its accepted double bonding character. At short distances, around $R_{eq} = 3.01$ a.u., it is normally described as being predominantly ionic, but turning to predominantly covalent at distances larger than about $2R_{eq}$. That is, in standard chemical terms, the LiH vibrations involve continuous changes of its bonding character, still difficult to be quantitatively explained. LiH becomes then a stringent test to the present theory. A previous Hir-I SAIM evaluation of the atomic charge amounts to ± 0.90 a.u.,²⁷ agreeing with some other previous calculations with different methods, including the QTAIM analysis.²⁸

The density was obtained with the aug-cc-pVQZ basis set. Figure 6 illustrates the CVSAIM partition of the density,

FIG. 6. Cut along the molecular axis z of the CVSAIM densities and effective potentials for LiH at equilibrium geometry. The shaded areas correspond to the electron fractions that follow the nuclear vibrations (cores). The vertical dashed line is a boundary between the core and valence parts of each CVSAIM (here the valence part of the Li CVSAIM almost vanishes).

the potentials, and the corresponding ranges that define the SAIM, which are again different for each nucleus. As long known, the valence electrons of Li and H have almost zero overlap. This feature led us previously to conclude for the lack of a valence (in the classical sense) electron fraction and that the cores would exchange electron fractions directly between themselves.²⁰ On the other hand, we see now that the Li core is really the full Li SAIM, having the recognized charge of +0.90 a.u. at $R_{eq} = 3.0$ a.u., but there is also a valence part (in the present quantitative sense) belonging exclusively to the H SAIM. The negative charge excess is transferred to the H SAIM as -0.38 a.u. on its core and -0.52 a.u. on its valence. At a larger distance, $R = 4.0$ a.u., the charges are +0.80 a.u. on Li, -0.31 a.u. on the H SAIM core, and -0.49 a.u. for its valence, the last still restricted to the H SAIM. The bonding picture that comes out is that as the atoms approach each other, the Li SAIM (only core) start loosing R -dependent electron fractions to the H SAIM, which divides it between core and valence parts. This picture is more detailed than the GVB (generalized valence-bond) energy partitioning

FIG. 5. Nonadiabatic corrections (cm^{-1}) to the vibrational levels of HeH^+ , *a*.²⁶

FIG. 7. Observed minus calculated vibrational energies LiH with different recipes for the effective nuclear masses, *a*,³⁹ *b*,⁴⁰ and *c*.²⁰

FIG. 8. Core electron fractions and reduced masses μ (in the insets) in atomic units versus the interatomic distance $R = z$. (a) H_2^+ , (b) H_2 , (c) HeH^+ , (d) LiH .

analysis of Fantuzzi and Chaer, which led to the conclusion that the bonding in LiH is predominantly covalent.²⁹ From the present point of view, the bond is actually ionic, since the Li SAIM does not contribute to valence, no matter the amount of charge transferred to the H SAIM. Common AIM approaches, including QTAIM and SAIM (without core-valence separation), give only the net charges on each atom. The possibility of this kind of analysis is a new outcome of the present approach.

The PEC is the same as that used in Ref. 20, including not only DBOCs but also relativistic corrections. The non-adiabatic corrections are obtained in the same way as for HeH^+ and are then added to the vibrational levels, leading to stringent agreement with experimental results, as shown in Figure 7. Various other approaches for effective masses are used for comparison. Note that the seemingly greater deviation from the experiments relative to the work in Ref. 20 can be elusive. In fact, comparison with experiments must be made carefully, since some experimental features and further effects (like quantum electrodynamics effects of the order of 10^{-1} cm^{-1}) are not accounted for. Particularly, all calculations point to an experimental loss of accuracy at large quantum numbers ν , in view of the ubiquitous oscillations. Anyway, the present results look extremely accurate one more time.

The advantage of the present approach over the older one²⁰ is the general and well-founded obtaining of core masses from SAIM. In consequence, no guessing for $\mu(R)$ or scaling of the corrections, as in Ref. 18, is now needed.

D. Further general data

Figure 8 shows the R -dependent core electron fractions for the four systems treated here. The insets show the resulting R -dependent reduced masses. Most interesting are the core fractions of H^+ and H in HeH^+ and LiH , respectively. Both present a peak at a distance lower than the equilibrium distance, at the expense of the decrease of the cores He and Li. At even smaller distances, both core masses get smaller, meaning that the valence fraction now increases. The limits $R \rightarrow 0$ and

$R \rightarrow \infty$ for all the systems are consistent with what is expected on physical grounds.

In the [supplementary material](#), the reader can find the vibrational energy data needed to calculate the nonadiabatic corrections for all the systems.

IV. DISCUSSION AND CONCLUSIONS

The first insights that non-adiabatic effects on the energy levels of well isolated PECs (or surfaces) were related to the dragging of electrons by the nuclei during vibrations or rotations refer back to the work of Herman and Asgharian,³⁰ where effective vibrational and rotational reduced masses were introduced in the nuclear equation. The connection of this idea with *ab initio* non-adiabatic theory was accomplished by Bunker and Moss³¹ and is in practice restricted to one-electron ions like H_2^+ . Further applications resorted (at least in part) to different heuristic arguments for each system,^{17,32–35} including previous works of our group.^{13,18,20} In the present paper, we develop a common approach for non-adiabatic corrections based on the role played by SAIM in the definition of the core electrons, namely, those that go along with the nuclei as they move.

SAIM were not originally defined from rigorous quantum chemical concepts but they avoid interpretative drawbacks presented by topological AIM. In fact, SAIM are quasi-spherically symmetrical and their densities spread over the full coordinate space, so they have non-zero superposition. Hence, SAIM are good choices for trying to connect the AIM behavior with molecular spectroscopic properties. Here we start from the definition of SAIM, obtain effective atomic potentials, and, with their help, identify the electron fractions that go along with the nuclei as they vibrate, the cores, which lead to the accurate evaluation of non-adiabatic corrections to the molecular energy levels.

Once we admit that the principle of minimum information entropy has a fundamental meaning, the present method results in an axiomatic (in opposition to the previous heuristic ones based on trial wavefunctions), also universal, way to obtain

effective masses and, consequently, non-adiabatic corrections. Of course, non-adiabatic corrections are not observables *per se*. Instead, they correct the approximate values of observables, the ro-vibrational energy levels of a molecule. They are, on the other hand, fully independent of the AIM concept, different from atomic charges, for example. They also have clear physical meaning, namely, they account for the dragging effect which the nuclei impose to a part of the electronic cloud, not accounted for by an adiabatic model.

The CVSAIM partition of the density gives further insights on the bonding mechanism of HeH^+ and LiH , not present in the usual population or the AIM analysis, and projects itself as a possible new tool for the chemical bonding analysis. The assertion of an ionic character to the bond in LiH shows that the CVSAIM point of view can recover classical concepts of chemical bonding from quantum chemistry calculations.

The results presented here address two important issues. The first concerns the quantum chemical foundations of CVSAIM. On the one hand, to develop the present CVSAIM analysis we started with the fractioning of the molecular Hamiltonian in core and valence parts, which is a basic assumption for the core-valence separation of motions in Ref. 13. On the other hand, it seems clear that those Hamiltonian fractions are quite difficult to conceive, since they should account for the molecular density in the form of Eq. (2). At present, we can say that, despite the lack of quantum chemical foundations, the CVSAIM analysis helped us to devise a general method to nonadiabatic corrections based on effective masses as well as furnish reliable new insights on chemical bonding. Furthermore, the level of theoretical-experimental agreement depends, among other aspects, on our ability in producing appropriate effective reduced masses. This point seems now to be well satisfied by the choice of core masses from the CVSAIM densities, so it addresses the second issue.

Are SAIM observables? In considering this question, we first recall that the theory in Ref. 13 was not devised to define SAIM at all. Instead, it was designed to theoretically explain and support the procedure of using effective core masses in non-adiabatic calculations. What we showed here is that the independent concept of SAIM, having superposed and non-superposed parts, fully agrees with that theory, so that it gives the best recipe so far to evaluate those effective masses. With “best recipe,” we mean here the one that, having a general character, leads to the agreement with experiments or accurate calculations within cm^{-1} accuracy. Our results then point to an indirect connection of CVSAIM with quantities directly connected to observables.

Whether CVSAIM are actual quantum objects or not is still a matter of discussion. The results in the present paper seem to suggest that the discussion on a real character of AIM could be resumed.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the numerical values of the vibrational energy levels for all the systems, calculated with both nuclear and effective core masses, as well as the corresponding non-adiabatic corrections to these levels.

ACKNOWLEDGMENTS

This work was supported by the Brazilian agencies Fapemig and CNPq. We acknowledge Professor Alex Alijah and Dr. Leonardo Diniz for useful discussions and suggestions.

- ¹P. Politzer and R. R. Harris, *J. Am. Chem. Soc.* **92**, 6451 (1970).
- ²F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Clarendon, Oxford, 1990).
- ³F. L. Hirshfeld, *Theor. Chim. Acta* **44**, 129 (1977).
- ⁴P. Bultinck, C. Van Alsenoy, P. W. Ayers, and R. Carbó-Dorca, *J. Chem. Phys.* **126**, 144111 (2007).
- ⁵K. Finzel, A. M. Pendás, and E. Francisco, *J. Chem. Phys.* **143**, 084115 (2015).
- ⁶T. C. Lillestolen and R. J. Wheatley, *Chem. Commun.* **45**, 5909 (2008).
- ⁷R. G. Parr, P. W. Ayers, and R. Nalewajski, *J. Phys. Chem. A* **109**, 3957 (2005).
- ⁸D. E. P. Vanpoucke, P. Bultinck, and I. Van Driessche, *J. Comput. Chem.* **34**, 405 (2013).
- ⁹T. Verstraelen, P. W. Ayers, V. Van Speybroeck, and M. Waroquier, *J. Chem. Theory Comput.* **9**, 2221 (2013).
- ¹⁰T. Verstraelen, S. Vandenbrande, F. Heidar-Zadeh, L. Vanduyfhuys, V. Van Speybroeck, M. Waroquier, and P. W. Ayers, *J. Chem. Theory Comput.* **12**, 3894 (2016).
- ¹¹S. Shahbazian, *Found. Chem.* **16**, 77 (2014).
- ¹²S. Fliszár, *Atomic Charges, Bond Properties, and Molecular Energies* (John Wiley & Sons, New Jersey, 2009).
- ¹³J. R. Mohallem, L. G. Diniz, and A. S. Dutra, *Chem. Phys. Lett.* **501**, 575 (2011).
- ¹⁴G. R. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1989).
- ¹⁵P. Bultinck, D. L. Cooper, and D. Van Neck, *Phys. Chem. Chem. Phys.* **11**, 3424 (2009).
- ¹⁶R. E. Moss and D. Jopling, *Chem. Phys. Lett.* **260**, 377 (1996).
- ¹⁷R. Jaquet, W. Cencek, W. Kutzelnigg, and J. Rychlewski, *J. Chem. Phys.* **108**, 2837 (1998).
- ¹⁸L. G. Diniz, A. Alijah, and J. R. Mohallem, *J. Chem. Phys.* **137**, 164316 (2012).
- ¹⁹L. G. Diniz, J. R. Mohallem, A. Alijah, M. Pavanello, L. Adamowicz, O. L. Polyansky, and J. Tennyson, *Phys. Rev. A* **88**, 032506 (2013).
- ²⁰L. G. Diniz, A. Alijah, L. Adamowicz, and J. R. Mohallem, *Chem. Phys. Lett.* **633**, 89 (2015).
- ²¹A. Alijah and G. Duxbury, *Mol. Phys.* **70**, 605 (1990).
- ²²M. W. Schimdt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).
- ²³L. Wolniewicz, *J. Chem. Phys.* **78**, 6173 (1983).
- ²⁴L. Wolniewicz, *J. Chem. Phys.* **103**, 1792 (1995).
- ²⁵W. Tung, M. Pavanello, and L. Adamowicz, *J. Chem. Phys.* **137**, 164305 (2012).
- ²⁶M. Stanke, D. Kedziera, S. Bubín, and L. Adamowicz, *Phys. Rev. A* **77**, 022506 (2008).
- ²⁷E. Francisco, A. M. Pendás, A. Costales, and M. García-Revilla, *Comput. Theor. Chem.* **975**, 2 (2011).
- ²⁸See <http://cccbdb.nist.gov/> for calculated atomic charges with various methods.
- ²⁹F. Fantuzzi and M. A. C. Nascimento, *J. Chem. Theory Comput.* **10**, 2322 (2014).
- ³⁰R. M. Herman and A. Asgharian, *J. Mol. Spectrosc.* **19**, 305 (1966).
- ³¹P. R. Bunker and R. E. Moss, *Mol. Phys.* **33**, 417 (1977).
- ³²W. Kutzelnigg, *Mol. Phys.* **105**, 2627 (2007).
- ³³R. Jaquet and W. Kutzelnigg, *Chem. Phys.* **346**, 69 (2008).
- ³⁴K. Pachucki and J. Komasa, *J. Chem. Phys.* **130**, 164113 (2009).
- ³⁵E. Mátyus, T. Szidarovszky, and A. G. Császár, *J. Chem. Phys.* **141**, 154111 (2014).
- ³⁶L. Wolniewicz and D. Poll, *Mol. Phys.* **59**, 953 (1986).
- ³⁷R. E. Moss, *Mol. Phys.* **89**, 195 (1996).
- ³⁸P. R. Bunker, C. J. McLarnon, and R. E. Moss, *Mol. Phys.* **33**, 425 (1977).
- ³⁹F. X. Gadea, F. Gemperle, H. Berriche, P. Villareal, and G. Delgado Barrio, *J. Phys. B: At., Mol. Opt. Phys.* **30**, L427 (1997).
- ⁴⁰S. P. A. Sauer, I. Paidarová, J. Oddershede, K. L. Bak, and F. G. Ogilvie, *Int. J. Quantum Chem.* **111**, 736 (2011).