

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244271841>

Evidences of molecular structure beyond the Born–Oppenheimer approximation: the model Hamiltonian

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · NOVEMBER 2004

Impact Factor: 1.37 · DOI: 10.1016/j.theochem.2003.12.055

CITATIONS

19

READS

37

1 AUTHOR:



[José Rachid Mohallem](#)

Federal University of Minas Gerais

75 PUBLICATIONS 703 CITATIONS

SEE PROFILE

Evidences of molecular structure beyond the Born–Oppenheimer approximation: the model hamiltonian

José R. Mohallem*

*Laboratório de Átomos e Moléculas Especiais, Departamento de Física, ICEx, Universidade Federal de Minas Gerais,
P.O. Box 702, Belo Horizonte, MG 30123-970, Brasil*

Abstract

It is shown that the adiabatic corrections in molecules constitute new evidences of atoms-in-molecules behavior, or molecular structure. A new interpretation of molecular geometry is introduced as well, based on point group symmetries displayed by the corrected electronic wavefunction.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Molecular structure; Born–Oppenheimer; Model Hamiltonian

1. Introduction

Molecular structure (MS) is, perhaps, the most fundamental concept of chemistry and molecular physics. It states that a molecule is made up of atoms linked by electron bonds. Molecular geometry (MG) is a derived and more restricted classical concept, established by the identification of nuclear positions with the minima of potential energy surfaces. Some decades ago a discussion started on the existence of quantum basis for the concept of MS (MG, actually) [1–7] based on the claim that MG is not an intrinsic property of the full molecular hamiltonian [1,2]. In fact, point group (geometrical) symmetries are known to be displayed only by the clamped-nuclei Born–Oppenheimer (BO) hamiltonian. On the other hand, the MS concept is easier to be advocated, and there has been a continuing effort to show that molecular properties can be partitioned in atomic contributions (atoms-in-molecules theories), but still resorting to the BO approximation. A recent example is the partition of the BO electron density, generating ‘topological atoms’ [8].

The BO approximation has a semi-classical character, with justifies the criticisms on the fundamental concepts of

MS and MG. In order to better support these concepts, we need to define them within post-BO quantum theories, as the variational adiabatic approximation [9]. The Born–Huang theory of molecules states that we must obtain electronic states in the clamped-nuclei BO approximation and then expand the total molecular wavefunction over this basis, being the expansion coefficients the nuclear wavefunctions. Elimination of center-of-mass motion with specification of a body-fixed-coordinate-system introduces prohibitive complications for polyatomic molecules [10] and mixes electronic and nuclear coordinates so that the BO approximation becomes less clear. Thus, the clamped-nuclei stage is commonly considered in the laboratory frame, a procedure not in accordance with the consideration of a normalizable Born–Huang total wavefunction (though this fact has been ignored in most polyatomic molecular calculations for decades). However, Kutzelnigg [11], based on diagonal-BO-correction (DBOC) calculations of Handy and collaborators [12,13], has shown that the inclusion of adiabatic corrections to the standard BO energy in the laboratory frame solve for these problems, no matter what set of coordinates is chosen for the correction. Everything works as if one had moved to the body-fixed-coordinate-system when the adiabatic correction is included, with no need of doing this explicitly. In what follows, an adiabatic approximation is taken as

* Fax: +55-031-499-5600.

E-mail address: rachid@fisica.ufmg.br.

any approximation in which a single product term of the Born–Huang expansion is considered. It generates different outputs, like DBOC, FNMC (see definition below), etc. depending on how the computations are further developed.

In the present work, we define a model hamiltonian by choosing a particular atomic form for the adiabatic correction, already explored in a semi-empirical sense in some previous applications [14–20]. We then discuss the exhibition of atoms-in-molecules (or MS) behavior by this hamiltonian. The exhibition of geometrical symmetries is discussed as well and a new interpretation for MG is proposed.

2. The model hamiltonian with atomic adiabatic corrections

For an n -electron atom, elimination of the center-of-mass motion generates the hamiltonian (in standard notation and atomic units, au)

$$H_{\text{at}} \approx - \sum_i^n \frac{\nabla_i^2}{2M} - \sum_i^n \frac{\nabla_i^2}{2} + V_{\text{at}}. \quad (1)$$

Here M is the mass of the atomic nucleus and V_{at} stands for all atomic Coulomb interactions. In fact, the exact form of the hamiltonian contains the further term

$$- \sum_{i \neq j}^n \frac{\vec{\nabla}_i \cdot \vec{\nabla}_j}{2M}$$

(called mass-polarization), which is very small, however, due to electron momenta correlation, and even vanish when calculated within a self-consistent-field model. The first and second terms of Eq. (1) could merge in just one with the introduction of the electron reduced mass

$$\mu = \left(1 + \frac{1}{M}\right)^{-1},$$

but here the role of the atomic correction operator

$$- \sum_i^n \frac{\nabla_i^2}{2M},$$

is to be emphasized.

We now propose a model molecular hamiltonian with a similar atomic form for the correction operator. Consider a molecule with m nuclei A, B, ... and n electrons i, j, \dots , with $n = n_A + n_B + \dots$. The hamiltonian in the laboratory frame is

$$H = - \sum_A^m \frac{\nabla_A^2}{2M_A} + - \sum_i^n \frac{\nabla_i^2}{2} + V_{\text{mol}} = - \sum_A^m \frac{\nabla_A^2}{2M_A} + H_{\text{BO}},$$

where V_{mol} stands for all Coulomb molecular interactions. We assume that we can eliminate the center-of-mass motion

of atomic sub-systems separately, so that the hamiltonian becomes

$$H_{\text{mol}} = - \sum_{j=1}^{n_A} \frac{\nabla_j^2}{2M_A} - \sum_{k=n_A+1}^{n_A+n_B} \frac{\nabla_k^2}{2M_B} + \dots - \sum_i^n \frac{\nabla_i^2}{2} + V_{\text{mol}}.$$

This hamiltonian, however, distinguish the electrons belonging to a particular atom. In order to correct for this improperly but, at the same time, keep the atomic character of the adiabatic correction, we postulate that each correction term will have vanishing matrix elements involving orbitals of different nuclei A and B. To stress this property, the operators are hereby symbolized by

$$- \sum_i^n \frac{\nabla_i^2}{2M_A} \delta_{AB}.$$

The model hamiltonian then assumes the form

$$H_{\text{mol}} = \sum_A^m \left(- \sum_i^n \frac{\nabla_i^2}{2M_A} \delta_{AB} \right) - \sum_i^n \frac{\nabla_i^2}{2} + V_{\text{mol}}. \quad (2)$$

This hamiltonian has a pure electronic form, so that the resulting approach is adiabatic. Now, self-consistent-field Hartree–Fock–Roothaan theory with this hamiltonian generates the empirical variational adiabatic molecular-orbital method already reported [19], in which the main feature is that the Fock matrix elements over nuclei-centered basis functions become

$$F_{\mu A \nu B}^{\text{new}} = F_{\mu A \nu B}^{\text{old}} + \frac{T_{\mu A \nu B}}{M_A} \delta_{AB}, \quad (3)$$

where μ, ν stands for basis functions features and T is the kinetic energy operator. Eq. (3), that has been used as a prescription, is now justified by the model hamiltonian 2. In Ref. [19], the difference $Q = E_{\text{ad}} - E_{\text{BO}}$, called finite-nuclear-mass-correction (FNMC) has been obtained with this method for some molecules (note that in our approach the adiabatic energy is variational, so that Q is not perturbative, that is, E_{BO} differs slightly from clamped nuclei energy). The FNMC is systematically larger than the DBOC by about 5–7% [19]. This quasi-coincidence becomes now more impressive in view of the present development, based on atomic model operators for the adiabatic correction. The immediate conclusion is that either FNMC or DBOC or, more generally, adiabatic corrections are, with good approximation, atomic properties of molecules. To further illustrate this conclusion, we consider the behavior of FNMC for some hydrides HX. Taking $M_X \gg M_H$, the corrections involving the H atom are dominating in the total FNMC and, relying on the atomic character of the correction, one can advance a linear relationship $Q \approx nQ_H$, where Q_H represents an individual term correction on the H atom. This is exactly what is displayed in Fig. 1, which becomes an interesting confirmation of the atomic character of the adiabatic correction.

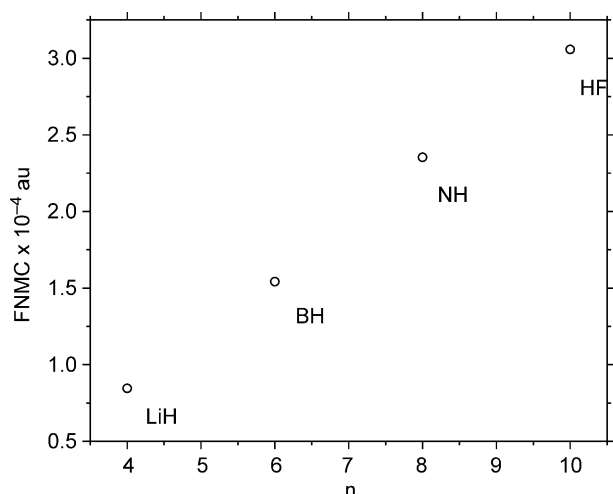


Fig. 1. Finite nuclear mass corrections, FNMC, versus number of electrons, n , for some hydrides.

3. Geometrical symmetries

In previous works [18,20], we have shown that hetero-isotopic molecules have their point group symmetries reduced relative to the homo-isotopic species in an analogous way as common heteronuclear molecules do. For example, being D the deuterium atom, D_2O displays all the C_{2v} symmetries of the common water molecule, while HDO loses the C_2 and σ_v symmetries, belonging to the C_s group [20]. Furthermore, the MOs of HD^+ [18] show, in a correlation diagram connecting united and separated atom limits, a reduction of symmetry from $D_{\infty h}$ to $C_{\infty v}$ (homonuclear to heteronuclear diatomic behavior), but still present symmetry conservation along the whole correlation diagram and the noncrossing rule holds as well. All of this is in accordance with the form we propose for the model hamiltonian 2, in which the appearance of the nuclear masses in the correction terms is responsible for the symmetry breaking. The conclusion is that in our post-BO molecular-orbital theory, the results *reinforces* the idea of geometrical symmetries, instead of destroying them (the common belief). On the other hand, it does not seem correct to think of MG as related to sharp minima of potential energy surfaces anymore. Indeed, the present approach can be extended to exotic molecules with very light nuclei (μ^+ , e^+ [14,16]), whose potential energy surfaces do not show sharp minima anyway (no equilibrium nuclear positions). Let us analyze more deeply the process of isotope symmetry reduction. Particularly for the HD^+ case, we have $[H,i] \neq 0$, where i represents the inversion symmetry operation. Physically, as the D nuclei attract the electron more strongly than the H nuclei, the electron density becomes asymmetric along the nuclear axis, as in a common heteronuclear molecule. But a fundamental difference is that this asymmetry is caused by kinetic effects, instead of potential energy effects of nuclear charges. Thus, on this level of theory, it becomes meaningless to speak of a classical

rigid nuclear frame. Instead, the point group symmetries become properties that must be asserted to the electronic distribution itself.

4. Final conclusions

While the total energy of a molecule shows a one-and two-center structure [21,22], the adiabatic correction shows a one-center nature, that is, it does not participate in the chemical bond. This conclusion is in accordance with the observation that the adiabatic correction does not affect bond lengths or vibrational frequencies, but is important for accurate calculations of energy differences, like dissociation energies [13]. Here it has been used as a sound to check atoms-in-molecules behavior. As for the geometrical properties of molecules, our results show that the concept of MG needs to be reviewed, since we have detected point group structures influenced by kinetic effects. This investigation will be pursued further in our group.

Acknowledgements

The author acknowledges Dr Cristina P. Gonçalves for her help with the calculations and CNPq by financial support. The main ideas presented here were developed in the waiting room of Dr Esperanza during a long surgery of my son's Tarik wisdom tooth, so their suffering was not in vain.

References

- [1] R.G. Woolley, Adv. Phys. 25 (1976) 27.
- [2] R.G. Woolley, J. Am. Chem. Soc. 100 (1978) 1073.
- [3] R.F.W. Bader, Y. Tal, S.G. Anderson, T.T. Nguyen-Dang, Isr. J. Chem. 19 (1980) 8.
- [4] P. Claverie, S. Diner, Isr. J. Chem. 19 (1980) 54.
- [5] M. Garcia-Sucre, M. Bunge, Int. J. Quantum. Chem. 19 (1981) 83.
- [6] J.G.R. Tostes, Theor. Chim. Acta 59 (1981) 229.
- [7] R.G. Woolley, J. Mol. Struct. (Theochem) 230 (1991) 17.
- [8] R.F.W. Bader, Atoms in Molecules, a Quantum Theory, Clarendon, Oxford, 1995.
- [9] R.T. Pack, J.O. Hirschfelder, J. Chem. Phys. 52 (1970) 521.
- [10] R.D. Bardo, M. Wolfsberg, J. Chem. Phys. 68 (1978) 2686.
- [11] W. Kutzelnigg, Mol. Phys. 90 (1997) 909.
- [12] N.C. Handy, Y. Yamaguchi, H.F. Schaefer III., J. Chem. Phys. 84 (1986) 4481.
- [13] N.C. Handy, A.M. Lee, Chem. Phys. Lett. 252 (1996) 425.
- [14] J.R. Mohallem, J. Phys. B: At. Mol. Opt. Phys. 32 (1999) 3805.
- [15] C.P. Gonçalves, J.R. Mohallem, Chem. Phys. Lett. 320 (2000) 118.
- [16] F. Rolim, J.P. Braga, J.R. Mohallem, Chem. Phys. Lett. 332 (2000) 139.
- [17] J.R. Mohallem, F. Rolim, C.P. Gonçalves, Mol. Phys. 99 (2001) 87.
- [18] C.P. Gonçalves, J.R. Mohallem, Chem. Phys. Lett. 367 (2003) 533.
- [19] C.P. Gonçalves, J.R. Mohallem, Theor. Chem. Acc. 110 (2003) 367.
- [20] C.P. Gonçalves, J.R. Mohallem, Chem. Phys. Lett. 380 (2003) 378.
- [21] H. Fischer, H. Kollmar, Theor. Chim. Acta. 16 (1970) 163.
- [22] I. Mayer, Chem. Phys. Lett. 332 (2000) 381.