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Molecular Shape Effects and Quantum Theory

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Certain features of the chemist's molecular structure model, viz. "size" and "shape", are retrieved even in the best non-adiabatic variational calculations thus far carried out for ground states of H_2^+ and H_2. Those features do not conflict with the full symmetry of exact molecular eigenstates, once they are properly understood as correlation effects.

Key words: Molecular shape: a correlation effect – Symmetries and shape of molecular eigenstates; H_2^+ and H_2.

1. Introduction

Recently, Woolley [1–3] has challenged the association of the "molecular structure" concept to the exact molecular eigenstates (ME) of the complete non-relativistic molecular Schrödinger equation. "Molecular structure has to be associated to those intrinsically time-dependent quantum states for which the identification between classical and quantum configurations can be made, since only then is it valid to relate notions of molecular structure to maxima in the molecular wave functions (wfs) in the position representation" [2]. Thus a ME "cannot have extension in space and time" [1, 2]. Two new important works, dealing with the same subject, have recently appeared. Bader [4], with very simple qualitative arguments, has claimed that the molecular structure concept may be recovered beyond the Born–Oppenheimer (BO) [5] approximation. Claverie and Diner [6] have argued further that even complete MEs may display certain features of the chemist's molecular structure concept, through correlation effects.

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Particularly, for complete ground MEs ($J = 0$), they claim that one may recover, through certain nuclear correlations, the rough molecular size that chemists associate to molecules; but they argued that one cannot retrieve in these kinds of states the also commonly accepted non-spherical molecular shape effects.

2. The Molecular Structure Model

Before any argumentation, we must first agree about a very definite "molecular structure" concept. Following Coulson [7] one may first define the concepts of *size* and *shape* of molecules (we will be dealing only with ground states of diatomic molecules):

Size – the boundary region around the point-like nuclei – separated by distances of the order of R_e, the "equilibrium internuclear distance" – with, say, a 99% chance of finding an electron inside, irrespective of the others. This information is imbedded in the famous one-electron density, $\rho(\mathbf{r}, R)$ [8], in which $\mathbf{r}$ is the electronic position and R the internuclear distance.

Shape – the particular shape displayed by $\rho(\mathbf{r}, R)$, at punctual nuclear arrangements around R_e.

As we will be dealing only with ground ($J=0$) MEs, the coordinate system was chosen so that ρ does not display explicitly the "molecular axis" (the axis containing the two nuclei) orientation. $\mathbf{r}$, throughout this work, is intended to depend upon such an orientation (given by the unitary vector, $\mathbf{R}/R$), i.e. the coordinate system is "rotating", with the molecular axis being one of the "rotating" axes.

Partially inspired by an important distinction made by Claverie and Diner [6], two different models of "molecular structure" may be proposed:

Model A (or the "static" model) – one retains only the "static" (i.e. in the sense of a stationary distribution) shape and size effects of the mono-electronic probability density mentioned above *plus* the "point-like" nuclear behavior. Fig. 1 displays a common picture of such a density in adiabatic calculations.

Model B (or the "dynamical" model) – it amounts to the above "static" model *plus* "dynamical" (in the sense of a non-stationary distribution) ingredients, viz.

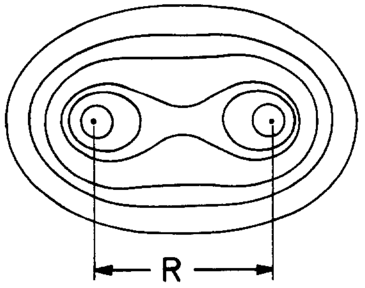

Fig. 1. Schematic surfaces of $\rho_0^{AD}(\mathbf{r}, R)$ = constant for the ground state of H_2^+; $R \approx R_e = 2$ Bohr

the rovibrational motion of the quasi-rigid nuclear framework followed instantaneously by the electronic "cloud" of Fig. 1, for example. Model B constitutes what can be named the *classical* molecular structure concept of quantum chemists.

As Claverie and Diner [6] forcefully argued, these dynamical ingredients of model B make it, right from the start, an inappropriate model for describing *exact* MEs and we will put it aside in this short communication.

On the other hand, it is worth noting, at least within the BO approach, that model A displays the famous chemist's shape-stability connection: particular (and practically equal) electronic clouds "looking" to nuclei with $R \approx R_e$ are strongly preferred in *energetical* terms.

Certain questions may be addressed now:

(2.1) Inspecting the best molecular non-adiabatic ground state calculations thus far carried out, how much of model A can be retrieved?

(2.2) In case model A fully persists in such calculations how can its non-spherical shape features be rationalized in a purely non-adiabatic language? Are they in accordance with the full symmetry of complete ground MEs?

Sects. 3 and 4 are intended to answer these two questions.

3. Two "Worked" Examples: H_2^+ and H_2

We are going to see that molecular size and shape effects – in the sense of model A – are retrieved even in the most accurate non-adiabatic calculations thus far carried out for ground states of H_2^+ and H_2.

We will align four argumentation steps; the fourth one will be conclusive.

(3.1) Following ordinary probability theory, Hunter [9, 10] and Hunter and Bishop [11] have shown that *exact* MEs (consider center of mass (CM) factorized out) may be *exactly* factorized in the product form:

$$\Psi(\boldsymbol{r}, R) = f(R) \cdot \phi(\boldsymbol{r}|R) \tag{1}$$

where Ψ is intended to describe a $J=0$ eigenstate; now $\boldsymbol{r}$ involves all (not one) electronic positions, but the remarks of Sect. 2 persist. $f(R)$ is the nuclear marginal amplitude and $\phi(\boldsymbol{r}|R)$ is the electronic conditional amplitude for a given R and a given orientation of molecular axis (see also the interesting paper by Wilson [12]). Consider now the BO vibrational, $f_{nm}^{AD}(R)$, and electronic, $\phi_n^{AD}(\boldsymbol{r}, R)$, wfs, where n and m represent, respectively, the electronic and vibrational quantum numbers. We can see that the two factors appearing in (1) are, respectively, the formal analogs of these two adiabatic wfs [11], despite physical and possible numerical differences. It is worth noting that the product form (1) is not restricted only to adiabatic states, conversely to what seems commonly suggested in the literature.

(3.2) The *exact* marginal amplitudes $f_{nm}(R)$ (we introduce here the same indices of adiabatic states for a mere comparative purpose among exact MEs and its corresponding adiabatic counterparts), are obtained from a reduced Schrödinger equation containing a pseudo potential $\mathrm{U}_{nm}(R)$ defined by:

$$\mathrm{U}_{mn}(R) = \langle\phi_{nm}(\boldsymbol{r}|R)H|\phi_{nm}(\boldsymbol{r}|R)\rangle_r / \langle\phi_{nm}(r|R)|\phi_{nm}(r|R)\rangle_r \tag{2}$$

where index $\boldsymbol{r}$ means "integration with respect to $\boldsymbol{r}$". Note that U_{nm}, just like $\phi_{nm}(\boldsymbol{r}|R)$ and conversely to the adiabatic potential curve, $E_n^{AD}(R)$, depends also on the "vibrational" index (we keep on using also the adiabatic terminology for the sake of simplicity); this is an indication that the molecular spectra cannot be decomposed i.e. the energy levels cannot be rigorously expressed as a sum of strictly independent electronic, vibrational, and rotational energy terms [9]. Now the nuclei "see" the exact instantaneous electronic coulombic field, not an averaged electronic field.

Particularly, in very accurate non-adiabatic treatments for H_2^+ [11] and H_2 [13] it was shown that the ground "potential" $U_{00}(R)$ is approximately equal to its adiabatic counterpart, $E_0^{AD}(R)$. Ref. 13 offered strongly convincing arguments showing that $\mathrm{U}_{0m}(m \neq 0)$ is heavily different from E_0^{AD} for certain values of R.

(3.3) Refs. 11 and 13 plus Kolos [14] and Wolniewicz [15] have shown for H_2^+ and H_2:

$$|f_{0m}(R)|^2 \approx |f_{0m}^{AD}(R)|^2$$

at least for the lowest "vibrational" non-adiabatic levels (from now on, $f_{nm}(R)$ and $\phi_{nm}(\boldsymbol{r}|R)$ will represent quasi-exact calculated amplitudes). Thus, particularly for H_2^+ and H_2, $|f_{00}(R)|^2$ "puts" the nuclei exactly where chemists always have put them for 55 years. In other words, nuclei persist strongly "confined" around 2 Bohr in H_2^+ and 1.4 Bohr in H_2; these privileged non-adiabatic values will be named with the same adiabatic symbol, R_e. This confinement amounts to a strong "localization" effect in the inter-nuclear distance, R, a *correlation* effect responsible for the nuclear "point-like" behavior–relative to electrons – in these molecules.

(3.4) From a practically exact non-adiabatic treatment for H_2^+ [16] plus steps (3.1), (3.2), (3.3), we may conclude ($R_e = 2$ Bohr):

$$|\Psi_{00}(\boldsymbol{r}, 2)|^2/|f_{00}(2)|^2 = |\phi_{00}(\boldsymbol{r}, 2)|^2 \approx |\phi_0^{AD}(\boldsymbol{r}, 2)|^2 \tag{3}$$

$$\begin{aligned}\int_0^\infty |\Psi_{00}(\boldsymbol{r}, R)|^2 dR &= \int_0^\infty |f_{00}(R)|^2 |\phi_{00}(\boldsymbol{r}, R)|^2\, dR \\ &= g(\boldsymbol{r}) \approx |\phi_0^{AD}(\boldsymbol{r}, 2)|^2\end{aligned} \tag{4}$$

where Ψ_{00} is the Bishop's ground state wf. Note that as H_2^+ contains only one electron: $|\phi_{00}(\boldsymbol{r}|R)^2 = \rho_{00}(\boldsymbol{r}, R)$. Both in (3) and (4) one practically recovers the same electronic "shape", $|\phi_0^{AD}(\boldsymbol{r}, 2)|^2$, of adiabatic calculations; but in $g(\boldsymbol{r})$ the internuclear distance has been integrated out. It must be stressed that in (4) only integration with respect to R was carried out, not with respect to the molecular axis orientation. It is also worth noting that the quasi-equality in (4) could be expected on purely qualitative grounds when one considers that $f_{00}(R)$ is a quasi-delta function, strongly peaked around 2 Bohr.

Combining (3) and (4) it may be concluded that the electron is strongly correlated with nuclei along the molecular axis; more specifically, with the nuclei *when they are found around 2 Bohr from each other along such an axis.* This gives us a three-body *correlation* effect. In other words, in what concerns its R-dependency we have $|\Psi_{00}(r, R)|^2 \approx 0$, except if $R \approx 2$ Bohr. In so far as the non-adiabaticity of such calculations can be pushed today, *this is the quantum basis*[1] *for the molecular shape effects – in the sense of model A, which is fully retrieved here – in* MEs *of one and two electrons stable molecules*: *a strong dynamical stabilizing intramolecular correlation effect,* i.e. an effect imposed by the particular Hamiltonian of those systems. On the other hand, the additional presence of electrons of parallel spins would merely provoke the appearance of the other crucial shape-making correlation: the Pauli's *kinematical* correlations.

These highly favoured – in probabilistic terms – shape-making correlations may also be formally related to the sharp minimum region of the non-adiabatic "potential" $\mathrm{U}_{00}(R)$ (see 3.2) around 2 Bohr. This correspondence completes the strong formal similarities of shape effects in the Bishop's quasi-exact treatment with adiabatic shape effects, i.e. one recovers even at this very accurate level the above mentioned "shape-stability" connection (Sect. 2).

Note however that $\mathrm{U}_{00}(R)$ (Eq. 2) is distinct from the non-adiabatic quantity suggested by Wilson [12], $E_{\mathrm{elec}}(R)$. Both are intended to be calculated with the same $\phi_{nm}(r|R)$, but the former "potential" involves the *exact* Hamiltonian" whereas the latter involves only the "electronic Hamiltonian", H_{el}. This procedure of Wilson is still problematic, at least in conceptual terms, because it envisages R as a c-number, not as a true quantum variable (just like in the BO approach).

4. Full Delocalization Versus Localizing Correlations in MEs

Once molecular size and non-spherical shape effects imbedded in Bishop's quasi exact wf were properly understood as correlation effects, one may conclude that these effects do not conflict with: (i) rotational invariance requirements for the $J = 0$ MEs; (ii) translational invariance requirements for the MEs.

(4.1) In the above discussed shape-making correlations the molecular axis plays the role of a mere correlation axis; such correlations do not create a preferential or "frozen" orientation in space: the orientation of that axis in space is fully isotropic ("fully delocalized") in accordance with the null angular momentum of ground MEs. This explains how such an isotropic distribution of molecular axis orientation may co-exist with *non*-spherical (many-body correlation) shape effects, without hurting the rotational symmetry of $J=0$ MEs.

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[1] Note that it is possible that even very accurate sets of non-adiabatic variational wfs are not suited for expanding *exact* MEs. But we think that this kind of limitation does not prevent us from labelling such treatments as "fully quantum" [17].

(4.2) The possibility of co-existence of "full delocalizations", required by the translational symmetry in atomic and molecular eigenstates, and "localizing correlations", was correctly pointed out by Claverie and Diner [6]. We would like to extend a bit further their argumentation, both in conceptual and observational terms, utilizing a very simple example. Consider the hydrogen atom with its six positional degrees of freedom in its ground state (1s). The position vectors for electron and nucleus may be represented by $\boldsymbol{r}_e$ and $\boldsymbol{r}_p$. Due to translational invariance the 1*s* state may be factorized in: $\Psi_{1s} = \exp(-i\boldsymbol{P}\cdot\boldsymbol{R}/h).\,\phi_{1s}(r)$, where $\boldsymbol{P}$ is the center of mass (CM) linear momentum, $\boldsymbol{R} = (M\boldsymbol{r}_p + m\boldsymbol{r}_e)/(M+m)$ is the CM position vector and $r = |\boldsymbol{r}_e - \boldsymbol{r}_p|$ is the *relative* distance between the two particles. Now, as a consequence of the translational symmetry, necessarily present in atomic and molecular eigenstates, the particles' positions are "fully delocalized", i.e. it is equally probable to find each particle – regardless of the other – anywhere in space (find the respective marginal densities for $\boldsymbol{r}_e$ and $\boldsymbol{r}_p$ and verify that they are constants). In the second set of coordinates one finds five "fully delocalized" degrees of freedom: the three CM coordinates (a consequence of the translational symmetry) and two angle variables (a consequence of the rotational symmetry in a state with null angular momentum) and a "localized" degree, *r*, with its well-known maximum at the "first Bohr orbit". As we have been speaking thus far independently of any act of measurement, we cannot associate to the "full delocalization" in space a greater or lesser rank of "actuality" as regards, for instance, the "point-like" protonic behavior. All these "properties" are equally "potential" (in the sense of Heisenberg [18, 19]). On the other hand, all possible positional details above mentioned – full delocalization in each particle position, full delocalization in $\boldsymbol{R}$ and two angles, localization in *r*, etc. – will be fully retrieved or "actualizable" in the same *complete* eigenstate, once one is able to *measure* the single distribution $|\Psi_{1s}|^2$ (with a proper position measuring device, which in particular strongly "confines" the system's particles to a much greater extent [20] as compared with the spreads or "uncertainties" of localized degrees of freedom – like *r* – in the system's wf *before* any measuring act).

5. Concluding Remarks

In so far as the non-adiabaticity of present calculations can be pushed today, the model *A* of molecular structure persists, at least in ground states of H_2^+ and H_2. The achieved shape-making correlations do not hurt any symmetry of complete MEs, even if one considers $J = 0$ eigenstates. It is perfectly reasonable to expect the extension of such results to the ground states of the common stable diatomic molecules, just as has been believed for 55 years. For certain polyatomic systems, at least, even ground states seem to display nuclear "large-amplitude vibrations", i.e. nuclei do not exhibit fully point-like correlations in all their famous 3*N*-6 "internal" degrees of freedom. In this case one cannot even retrieve model A of molecular structure in such states.

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References

1. Woolley, R. G.: Adv. Phys. **25**, 27 (1976)
2. Woolley, R. G.: J. Am. Chem. Soc. **100**, 1073 (1978)
3. Woolley, R. G.: Isr. J. Chem. **19**, 30 (1980)
4. Bader, R. F. W., Tal, Y., Anderson, S. G., Nguyen-Dang, T. T.: Isr. J. Chem. **19**, 8 (1980)
5. Born, M., Oppenheimer, J. R.: Ann. Phys. **84**, 547 (1927)
6. Claverie, P., Diner, S.: Isr. J. Chem. **19**, 54 (1980)
7. Coulson, C. A.: The shape and structure of molecules. Oxford: Clarendon Press 1973
8. Smith, V. H., Absar, I.: Isr. J. Chem. **16**, 87 (1977)
9. Hunter, G.: Intern. J. Quantum Chem. **S8**, 413 (1974)
10. Hunter, G.: Intern. J. Quantum Chem. **9**, 237 (1975)
11. Bishop, D. M., Hunter, G.: Mol. Phys. **30**, 1433 (1975)
12. Wilson, E. B.: Intern. J. Quantum Chem. **S13**, 5 (1979)
13. Czub, J., Wolniewicz, L.: Mol. Phys. **36**, 1301 (1978)
14. Kolos, L., Wolniewicz, L.: J. Chem. Phys. **41**, 3674 (1964)
15. Wolniewicz, L.: J. Chem. Phys. **45**, 515 (1966)
16. Bishop, D. M., Cheung, L. M.: Intern. J. Quantum Chem. **15**, 517 (1979)
17. Tostes, J. G. R.: Chem. Phys. Letters **68**, 183 (1979)
18. Bohm, D.: Quantum theory. Englewood Cliffs, N. J.: Prentice-Hall 1951
19. Ballentine, L. E.: Rev. Mod. Phys. **42**, 358 (1970)
20. Landé, A.: Am. J. Phys. **37**, 541 (1969)

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