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Application of the Virial Theorem to the Study of Molecular Electronic Wave Functions

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With aid of the virial theorem formulated for the energy differences of two electronic states some theorems on the wave functions of diatomic molecules have been proven. It is shown how proper Rydberg states can be distinguished from other electronic states with a diffuse outer orbital by virtue of the virial theorem and that a singlet-triplet pair of excited states cannot have the same equilibrium geometry and identical orbitals simultaneously. Furthermore if the two states have the same dissociation limit a theorem on the differences of the kinetic and the potential energy can be derived which allows an understanding of the shape of the electronic wave functions. As an application the wave functions and the ordering of the lowest states of H_2^+ and H_2 have been discussed.

Key words: Virial theorem – Electronic wave function, shape of the ~

1. Introduction

Recently different authors have pointed out that the common interpretation of Hund's rule can be shown to be incomplete [1–8]. The virial theorem has been invoked in some of these discussions [3, 4, 7]. This theorem is a basic mechanical law which states that the expectation values of the kinetic energy T, the potential energy V and the total energy E are connected by the relations (1a, b):

$$T = -E \tag{1a}$$

$$V = 2E \tag{1b}$$

if we consider a force-free atomic or molecular system held together by Coulombic forces. (1b) follows from (1a) and $T + V = E$; for T, V, E the energies of any state can be substituted. For molecules the total energy sometimes is replaced by the total electronic energy T_{el}, V_{el}, E_{el} and the virial theorem has a somewhat different form (see Sect. 2). Hereby however the separability of electronic and nuclear motion and the existence of potential surfaces are assumed.

Consider two different bound states of an atom not degenerate with one another. If the two states do not arise from the same electronic configuration, within the terminology of the MO approximation we can say that in the higher state higher lying orbitals are occupied which are empty in the lower state. Higher lying atomic orbitals are in general characterised by a greater number of nodes and therefore the kinetic energy of the electrons should increase. On the other hand the virial theorem (1a) requires that the higher state has less kinetic energy than the lower one (E is always negative). As a consequence excited atomic orbitals are much more spread out than low lying ones for so they can have more nodes and less kinetic energy (a reduced curvature) at the same time.

This result also supports the estimation of Ahlrichs for the long-range behaviour of electronic wave functions [9–11] saying that any bound state wave function upon removal of one electron to infinity decays faster than an exponential function with an exponent proportional to the square root of the ionisation energy of the state in question. One is tempted to conclude hereupon that a bound electronic wave function is the more diffuse the closer its energy lies to the ionisation limit. This conclusion applies for Rydberg-like systems (see Sect. 3) but we shall show a counterexample in Sect. 4. Let us turn now to two states belonging to the same electronic configuration like ^1P and ^3P of He ($1s$) ($2p$). Here in contrast to the simple MO picture the $1s$ and $2p$ orbitals cannot be identical for both states but in the higher state (^1P) there is an expansion, in the lower one a contraction of the $2p$ orbital because of the virial theorem (1a) and there is more electron repulsion in ^3P [2, 5, 20, 21]. With identical orbitals both states would have the same kinetic and nuclear attraction energy and the singlet-triplet splitting is determined by the difference of the electron repulsion. Although this crude picture predicts a wrong partitioning of the total energy, it has been shown by Katriel [4] that the exchange integral ($1s\,2p/2p\,1s$) determines the sign and to a smaller extent also the magnitude of the singlet-triplet splitting. The variational principle acts as a "driving force" and yields in general useful results for the total energy even if applied to trial functions with insufficient flexibility. The virial theorem on the other hand allows a qualitative discussion of the shape of the correct wave function but it cannot replace the variational principle as a tool for calculating wave functions.

2. Molecules

Application of the virial theorem to molecules suggests a restriction to diatomic molecules. Because of the appearance of two further parameters – the interatomic distance R and the slope of the potential curve $E' = dE/dR$ [12, 13] – it is more difficult to draw precise conclusions than in the atomic case. However Ruedenberg has successfully studied the binding properties of H_2^+ with the aid of the virial theorem [14, 15]. For small R we have the additional drawback that the results cannot be compared with the limiting case of the "united atom" unless the nuclear repulsion is subtracted from the energy expression. Some of these difficulties can be avoided if we formulate the virial theorem for the energy differences ΔE, ΔV, ΔT of two different electronic states. Δ means hereby the difference "upper state minus lower state"; hence $\Delta E \geqslant 0$ (we shall not consider a case of crossing potential curves). The virial theorem reads now [7]

$$\Delta T = -\Delta E - R\Delta E' \tag{2a}$$

$$\Delta V = 2\Delta E + R\Delta E' \tag{2b}$$

From (2) we see at once – since R is positive – that diverging potential curves ($\Delta E' > 0$) lead to a more negative ΔT and a more positive ΔV than would be the case for an atom with the same ΔE, whereas converging potential curves ($\Delta E' < 0$)

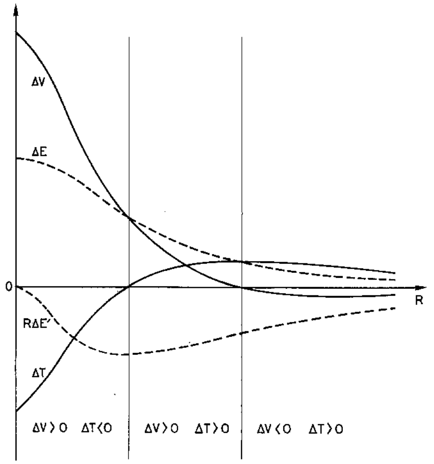

Fig. 1. Schematic illustration of Eq. (2) for the case of two states with the same dissociation limit. The decomposition of the total energy difference ΔE into potential and kinetic energy ΔV, ΔT is shown as a function of R. The atomic region (left), molecular region (middle) and the region of nearly separated atoms (right) are indicated.

yield a less negative ΔT and a less positive ΔV. This second case is of interest because in contrast to the virial theorem for atoms $\Delta T > 0$ or $\Delta V < 0$ can also occur. In fact it follows from (2) that $\Delta T = 0$ if $\Delta E(R)$ vanishes proportional to R^{-1} or that $\Delta V = 0$ if ΔE goes proportional to R^{-2}. Let us therefore consider the special case of two potential curves leading to the same dissociation limit (e.g. ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ of H_2, see [16–18]). The shapes of the curves for large R depend on the fragment charges: Ion pairs show R^{-1} curves and attraction even at large distances whereas neutral fragments will have curves which are roughly proportional to $\exp(-AR)$ (attraction or repulsion). The same exponential decrease of ΔE applies for ions dissociating into a charged and a neutral fragment. Therefore for such a pair we can divide the range of possible R values into three regions (see Fig. 1). An "atomic" region near $R = 0$ is characterised by $\Delta T < 0$, $\Delta V > 0$. For sufficiently large R we have a region of "nearly separated atoms" with $\Delta T > 0$, $\Delta V < 0$ and between these two there is a "molecular region" with $\Delta T > 0$, $\Delta V > 0$ (for $\Delta T + \Delta V = \Delta E \geqslant 0$ everywhere). For fluctuating ΔE even more changes of the signs of ΔT and ΔV could occur. In the limit of dissociation ($R = \infty$) we have from (2) $\Delta E = \Delta V = \Delta T = 0$ since $\Delta E'$ goes to zero much faster than R^{-1}.

The meaning of these three regions can be explained as follows: In the atomic region the electrons see rather a nearly pointlike positive charge than an extended nuclear skeleton. The potential curves are mainly determined by the nuclear repulsion, so $\Delta E' \sim 0$. Therefore the electronic wave functions behave like atomic functions: the higher the energy of a (bound) state, the lower is its kinetic energy. This implies that the higher lying components of a given electronic configuration (e.g. singlets) show orbital expansion compared with the lower lying components (triplets) similar to atoms [5, 7, 19].

The situation in the molecular region corresponds to the simple molecular orbital (MO) picture where the higher lying orbital and hence in general the higher lying state are characterised by a larger number of nodes and therefore by a higher kinetic energy. Furthermore in the MO model also the potential energy is often higher (less negative) for the higher lying orbital as can be seen considering e.g. the antibonding *pi* orbital of a polar molecule like H_2CO where the electron density is forced by the orthogonality condition to be higher at the less attractive carbon atom. In the molecular region an electronic excitation implies a smaller rearrangement between kinetic and potential energy than in the other two regions because only here Eq. (3) can be used with the equality sign:

$$|\Delta T|+|\Delta V|\geqslant|\Delta E|. \tag{3}$$

The conditions in the third region with large R contradict both the MO model and the simple form of the virial theorem (1). We shall discuss this case with the aid of two examples (H_2^+ and H_2) in Sect. 4.

The division of the R values into three regions as given above is not absolute but depends on the choice of the two converging potential curves. Such a treatment could be extended by considering a pair of curves with different dissociation limits if only the energy changes relative to $\Delta E(\infty)$, $\Delta T(\infty)$, $\Delta V(\infty)$ are treated. For this definition of the energy differences Eq. (2) can be applied since

$$\Delta E(\infty)=-\Delta T(\infty)=0.5\Delta V(\infty). \tag{4}$$

3. Rydberg States and Equilibrium Geometries

It has to be pointed out that the minima of the potential curves do not necessarily belong to the molecular region. Both the $1^1\Pi_u$, $1^3\Pi_u$ states of H_2 discussed in [7] have nearly the same equilibrium distance of 1.95 bohr. Therefore we have $\Delta E'(R_e)\sim 0$ and hence R_e belongs to the atomic region. The associated molecular region is at twice this distance around 4 bohr. In this case the term "atomic region" seems to be misleading but in fact it is not since these states are Rydberg states whose potential curve is largely dictated by the properties of the corresponding ion. H_2^+ has indeed its equilibrium at 2.00 bohr [22].

If a Rydberg state is defined as an electronic state where one electron is weakly bound in the field of an ionic core and occupies a hydrogenlike orbital which is much larger than the other occupied orbitals and the nuclear skeleton then the bonding energy e and the kinetic energy t of the Rydberg electron should approximately obey the atomic virial theorem

$$t=-e. \tag{5}$$

(Note that e is not a Hartree-Fock orbital energy but the total kinetic and potential energy of the Rydberg electron in the field of the core). On the other hand neglecting the perturbation of the core due to the presence of the Rydberg electron we can estimate the energy difference between the free ion and the Rydberg state as $\Delta E(R)=-e(R)$, hence $\Delta E'(R)=-e'(R)$ and $\Delta T(R)=-t(R)$. Putting these expressions into (2a) we get

$$-t(R)=e(R)+Re'(R) \tag{6}$$

and from (5) and (6) follows $Re'(R)=0$, i.e. because of $e'(R)=0$ the potential curve of the Rydberg state is predicted to be parallel to the curve of the ion. This result is of course due to assumption (5) and the above definition of a Rydberg state. But it may be helpful in order to distinguish Rydberg states from other electronic states with a diffuse outer orbital which however does not behave like an atomic orbital. Examples for such states are provided e.g. by the bound states of H_2^+ [24] whose potential curves are certainly not parallel to the curve of the parent ion since the latter is a repulsive $1/R$ curve. The other way round: whenever the potential curve of an electronic state with one weakly bound electron is not parallel to the curve of the parent ion, then the effective field and the orthogonality conditions which determine the shape of the outer orbital deviate sensibly from spherical symmetry and we have no proper Rydberg state.

Furthermore let us consider two electronic states of the same orbital configuration, e.g. a singlet-triplet pair. As a consequence of the virial theorem (2) the two states cannot have simultaneously parallel potential curves and, for a given R, an identical space part of the wave function. Especially the assumption of identical orbitals contradicts the assumption of identical equilibrium distances $R_{1,e}=R_{2,e}$. The first condition yields $\Delta T(R_e)=0$, the second one $\Delta E'(R_e)=0$ and their combination contradicts Eq. (2) if $\Delta E(R)\neq 0$. It follows that the above assumptions can be justified for small ΔE. If there is a large singlet-triplet splitting on the other hand different orbitals are to be expected for the two states since the triplet state tends to maximise the (stabilising) exchange integral whereas the singlet will minimise it in order to have a low energy. The molecular situation is realised if

$$\Delta E(R) \leqslant -R\Delta E'(R) \leqslant 2\Delta E(R). \qquad \text{(7a, b)}$$

Here the first inequality follows from $\Delta T \geqslant 0$, the second one from $\Delta V \geqslant 0$ by virtue of (2). Hurley [23] has shown that indeed

$$\Delta E(R) = \Delta E(R_e) \cdot R_e/R \qquad \text{(7a')}$$

is a good approximation near the equilibrium in many cases. This equation is equivalent to (7a). (7b) yields

$$\Delta E(R) = \Delta E(R_e)(R_e/R)^2. \qquad \text{(7b')}$$

The above considerations are suitable also for larger molecules. In the polyatomic case the virial theorem has a more complicated form depending on the internal coordinates and the corresponding derivatives of the potential surfaces. But at the equilibrium geometry the conditions (2) can still be applied.

4. Application of the Virial Theorem to H_2^+ and H_2

In this section we shall study the question to what extent the shape of the electronic wave functions of H_2^+ and H_2 are dictated by the virial theorem. The examples of these species are especially well suited because for both very accurate investigations, also for large interatomic distances, are available [15, 16, 18, 24]. In both cases we have a pair of potential curves converging to the same fragmentation limit: ${}^2\Sigma_g^+$, ${}^2\Sigma_u^+$ going to $H(1s)+H^+$ for H_2^+ and ${}^1\Sigma_g^+$, ${}^3\Sigma_u^+$ going to $H(1s)+H(1s)$ for H_2 such that the requirements of Sect. 2 are fulfilled.

According to the calculations of Ruedenberg *et al.* [14, 15] the molecular region of the $^2\Sigma_g^+$, $^2\Sigma_u^+$ pair of states of H_2^+ extends from 1.5 bohr to 2.8 bohr, the minimum of the lower curve being at 2.0 bohr. For shorter distances the energy partitioning is qualitatively the same as in the united atom He^+ : The diffuse $2p\sigma_u$ orbital has less kinetic energy and less nuclear attraction than the $1s\sigma_g$ such that $\Delta T<0$, $\Delta V>0$. For large distances the inverse is true as predicted in Sect. 2. σ_u is more contracted to the nuclei, hence $\Delta V=\Delta V_{en}<0$, i.e. there is less nuclear attraction in the lower state than in the higher one. Qualitatively the surplus of kinetic energy in the higher state can be attributed to the node of the σ_u orbital. Here we have a case where the electronic wave function of the energetically lower state is more diffuse than the function of the upper state. In the molecular region we have still $\Delta T>0$ although the σ_u orbital is now expanded and σ_g contracted such that $\Delta V>0$ (more nuclear attraction for σ_g). For the $^2\Pi_u$, $^2\Pi_g$ pair of states of H_2^+ arising from $H^+ + H(2p\pi)$ the same conclusions can be drawn [25].

For H_2 a qualitative discussion of the shape of the wave function is more difficult since the kinetic energy is now distributed over two electrons, the potential energy consists of nuclear attraction and electron repulsion and the correct wave function has a complicated form because of electron correlation. Analysis of the results of Kolos and Wolniewicz [16] reveals a molecular region of the $^1\Sigma_g^+$, $^3\Sigma_u^+$ pair of states extending from 1.4 bohr ($\Delta T=0$) to 2.1 bohr ($\Delta V=0$). Our qualitative discussion shall be based on the extended Hartree–Fock function of Bowman, Hirschfelder and Wahl [18] and following Mulliken [17] we call the $^1\Sigma_g^+$ state N, the $^3\Sigma_u^+$ state T:

$$\Psi_N=\lambda \det |\sigma_g\alpha\ \sigma_g\beta|-\mu \det |\sigma_u\alpha\ \sigma_u\beta| \tag{8a}$$

$$\Psi_T=2^{-1/2} \det |\sigma_g\alpha\ \sigma_u\beta|-2^{-1/2} \det |\sigma_u\alpha\ \sigma_g\beta| \tag{8b}$$

The coefficients λ, μ are tabulated e.g. in Ref. [18]: at the H_2 equilibrium $\lambda\sim 0.99$, $\mu\sim 0.11$, for infinite separation $\lambda=\mu=2^{-1/2}$. In Ref. [18] the σ_g, σ_u orbitals of Ψ_N and Ψ_T are drawn for three different situations with $R=0$, $R=1.5$ bohr and $R=5$ bohr. Note that these three distances represent just the three regions defined above. Calling η the orbital exponent of the atomic orbitals we observe that for

$$R=0 \qquad \eta(\sigma_g,T)\gtrsim\eta(\sigma_g,N)\sim\eta(\sigma_u,N)\gg\eta(\sigma_u,T) \tag{9a}$$

$$R=1.5\text{ bohr} \qquad \eta(\sigma_g,T)\sim\eta(\sigma_g,N)<\eta(\sigma_u,N)\gg\eta(\sigma_u,T) \tag{9b}$$

$$R=5\text{ bohr} \qquad \eta(\sigma_g,T)\sim\eta(\sigma_g,N)\sim\eta(\sigma_u,N)\sim\eta(\sigma_u,T)\sim 1. \tag{9c}$$

For short and medium distances the T state σ_u orbital is distinctly more diffuse than the σ_u orbital of N (9a, b). Furthermore near the united atom T has a somewhat more contracted σ_g than N (9a). For sufficiently large separation the atomic orbitals are all nearly equal (9c).

(9a) is the consequence of the virial theorem for atoms as discussed above. If R increases from 0 to 1.5 bohr all the orbitals expand because of the separation of the nuclear charges and hence there is a decrease of the kinetic energy. But this decrease is much more significant for the N state because the σ_g orbital which is doubly occupied in N and singly occupied in T expands faster than σ_u [18]. Hence at $R=1.5$ bohr the N state has less kinetic energy than T such that $\Delta T>0$. For large separations both orbitals have nearly the same weight in both wave functions (8) and also the same dimensions (9c). However a simplified wave function putting $\lambda=\mu$ and identical orbitals σ_u, σ_g in (8a, b) for large but not infinite distances like e.g. the Heitler-London function [26] yields $\Delta T=0$, $\Delta V=\Delta V_{ee}$ in contradiction to the virial theorem (Sect. 2). Furthermore both the Heitler-London and the more flexible Wang functions (σ_g, σ_u varied independently for both states [27, 28]) predict a crossing of N and T at $R\sim 50$ bohr [29, 30], violating a theorem probably due to Wigner (see [31]) which states that a two electron system has always a singlet ground state. But already the wave functions (8) with $\lambda\gtrsim\mu$ for all finite distances conform to the requirements of the virial theorem even if identical orbitals for both states are assumed in the region of nearly separated atoms. Due to correlation the σ_g orbital has a somewhat increased and σ_u a reduced weight in Ψ_N compared to Ψ_T such that $\Delta T>0$ for σ_u has more kinetic energy than σ_g. In contrast to H_2^+ there is no need for an expansion of the ground state orbitals since $\Delta V\sim\Delta V_{ee}<0$ even for identical orbitals: In the triplet state there is less electronic repulsion because of the Fermi hole which keeps the electrons apart from each other, conforming to the common interpretation of Hund's rule. However, due to correlation effects the singlet state has less kinetic energy and is more stable than the triplet state such that Hund's rule fails in this situation.

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