



An extension of the virial theorem for general wave functions

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Received 26 August 2007; in final form 5 October 2007

Available online 12 October 2007

Abstract

An extension of the virial theorem in the Born–Oppenheimer framework is presented, which is valid for arbitrary (not necessarily variational) wave functions built up by using finite local one-electron basis sets. It permits to define explicitly the terms causing deviations from the ‘ideal’ virial ratio; the standard formulations of the virial theorem can also be obtained from it as special cases.

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1. Introduction

The virial theorem is one of the general results of large conceptual importance which are, however, difficult to apply in practical applications because the conditions of their fulfillment are too strict to be easily satisfied. In addition, within the framework of the commonly used Born–Oppenheimer approximation the classical form of the virial theorem for Coulombic systems

$$2T + V = 0 \quad (1)$$

is valid only in the stationary points of the potential surface. In (1) T is the expectation value of the kinetic energy of the electrons and V is that of the total potential energy of the system (including nuclear–nuclear repulsion). Outside the stationary points, one should add an additional term – Slater [1] identified it the classical virial of the external forces keeping the nuclei fixed – thus one has [1,2]

$$2T + V + \sum_x \vec{R}_x \frac{\partial E}{\partial \vec{R}_x} = 0 \quad (2)$$

This form of the virial theorem is valid for the exact solutions [3], as well as some sufficiently general variational wave functions.

As Löwdin pointed out, the fulfillment of these relationships is a necessary (but not sufficient) condition that the wave function is of high quality [2]. Approximate wave functions used in everyday practice are usually not fulfilling these requirements and do not satisfy (1) or (2). This is the case, because one usually uses atom-centered basis sets, without independent optimization of the centers and of the exponents of the individual primitive basis function (by using floating basis sets and optimized exponents, one can quickly approach [4] the Hartree–Fock limit, for which the virial theorem holds). Nonetheless, the ‘virial ratio’ $-V/T$ is often sufficiently close to two, that the relationship

$$E \cong -T \quad (3)$$

can be used for obtaining a quite meaningful approximate energy partitioning for molecules at their stationary geometries [5–7].

The aim of the present Letter is to present an extension of the virial theorem within the Born–Oppenheimer framework, which is valid for *arbitrary* (not necessarily variational) wave functions built up by using finite local one-electron basis sets. It permits to define explicitly the terms causing deviations from the ‘ideal’ virial ratio; the standard formulations of the virial theorem can also be obtained from it as special cases. An analytical example and some numerical ones will also be shown to illustrate the result.

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2. Extension of the virial theorem

Let us consider a molecular system within the framework of the Born–Oppenheimer approximation, described with an approximate wave function written down by using a finite basis set¹. Neither the wave function nor the basis functions are required to be fully optimized. The nature of the wave function needs not to be specified here, e.g., it can be that obtained by solving the HFR equations, but also a correlated one. A given electronic wave function Ψ of the system depends on the electronic coordinates $\{\vec{r}_i\}$ as independent variables, as well as on the following parameters: positions of the centers of the basis functions $\{\vec{P}_q\}$ which may, or may not, coincide with either of the nuclei, and the scaling factors $\{\zeta_j\}$ of the (primitive) basis orbitals (as the positions of the centers are treated independently, the nuclear coordinates do not represent explicit parameters of the wave function). The scaling factors are understood in the sense, that each (primitive) basis function $\chi(\vec{r}_i)$ contains terms of structure $\zeta_j \vec{r}_{iq} = \zeta_j(\vec{r}_i - \vec{P}_q)$; this means that ζ_j can be an exponent of a Slater-function or the square root of an exponent of a Gaussian function. There are, of course, also different constants like contraction coefficients, orbital expansion coefficients, CI coefficients or CCA amplitudes which determine the functional form of the given wave function; they need not be considered explicitly, but are included in the notion of the ‘given’ electronic wave function. Thus the energy of the system described with the given wave function will be considered as depending explicitly on the parameters $\{\vec{R}_x\}$, $\{\vec{P}_q\}$ and $\{\zeta_j\}$.

Let us now consider a uniform scaling of the system, e.g., compression of it along all spatial directions. It is to be stressed that in this case one has to treat the independent variables (electronic coordinates \vec{r}_i) of the wave function Ψ and its parameters (nuclear coordinates \vec{R}_x , centers \vec{P}_q and scaling factors ζ_j of the basis functions) in a conceptually different manner. In fact, the usual scaling transformation in which one replaces the electronic coordinates \vec{r}_i in the arguments of Ψ by the scaled $\vec{\rho}_i = \eta \vec{r}_i$ corresponds to stretching the vectors of independent variables; if $\eta > 1$, that leads not to expansion but to compression of the system: for instance, a given maximum or minimum of $|\Psi|^2$ will be reached at a smaller $\vec{r}_i = \vec{\rho}_i/\eta$ value. Accordingly, in order to scale (compress) the system without distorting it, one has to reduce in the same proportion the vectors \vec{R}_x and \vec{P}_q describing the positions of the nuclei and of the centers of the basis orbitals, respectively, i.e., change them to \vec{R}_x/η and \vec{P}_q/η and stress the individual \vec{r}_{iq} -s separately, by replacing them with $\vec{\rho}_{iq} = \eta \vec{r}_{iq}$; the scalars $\{\zeta_j\}$ should be left unchanged. We assume that the normalization of the wave function is kept unchanged

during the compression (the above considerations are in agreement with the remark made in Ref. [8]: ‘a particular scaling of the wave function is transferred to an equivalent inverse scaling of the operator’).

The effect of scaling on different quantities in the framework of the Born–Oppenheimer separation has been discussed by Löwdin [2] (also see, e.g., [9]). In our case – as we distinguish between the centers of the basis orbitals \vec{P}_q and the positions of the nuclei \vec{R}_x – his equations can be written as

$$\begin{aligned} T(\eta, \vec{P}) &= \eta^2 T(1, \eta \vec{P}) \\ V(\eta, \vec{P}, \vec{R}) &= \eta V(1, \eta \vec{P}, \eta \vec{R}) \end{aligned} \quad (4)$$

here the first arguments correspond to the scaling coefficients of the electronic coordinates, the second and third ones stay for all the positions of the basis orbitals and of nuclei, respectively².

Applying these equations to the geometric parameters $\vec{P}'_q = \vec{P}_q/\eta$; $\vec{R}'_x = \vec{R}_x/\eta$, and omitting the primes, we may also write

$$\begin{aligned} T(\eta, \vec{P}/\eta) &= \eta^2 T(1, \vec{P}) \\ V(\eta, \vec{P}/\eta, \vec{R}/\eta) &= \eta V(1, \vec{P}, \vec{R}) \end{aligned} \quad (5)$$

These results can be compactly written as

$$T(\eta) = \eta^2 T(1) \quad (6)$$

and

$$V(\eta) = \eta V(1) \quad (7)$$

where $T(1)$, $V(1)$ are the values of the kinetic and potential energy before the uniform scaling (i.e. corresponding to the value $\eta = 1$)³.

These results agree with the behaviour predicted by the general theory [3,10] for the change of the kinetic and potential energy (Coulombic systems) under uniform scaling, if the normalization of the wave function is kept unchanged; they are direct consequences of the fact that both the kinetic and the potential energy are homogeneous functions of the coordinates (of the order -2 and -1 , respectively). It is easy to see that in our case Eq. (6) indeed applies for the kinetic energy of the electrons and Eq. (7) to all the potential energy components, as we have performed a uniform scaling (compression) of the overall system by a factor of η . According to Eqs. (6) and (7), the total electronic energy (including the nuclear repulsion) as function of η becomes in the case of uniform scaling (compression)

$$E(\eta) = \eta^2 T(1) + \eta V(1) \quad (8)$$

¹ Our considerations are not necessarily valid for some less conventional basis functions as multicenter ones or plane waves, or for wave functions containing the interelectronic distances explicitly (we are grateful to a Referee for calling attention to this point).

² The kinetic energy of electrons does not explicitly depend on the positions of the nuclei, so they are not indicated in its expression.

³ Eqs. (6), (7) also show that the scaling transformation with $\eta > 1$ corresponds to a compression (and not to an extension) of the system: both the kinetic and the potential energies increase in absolute value.

Accordingly, we have for the derivative of the energy in the point $\eta = 1$

$$\left. \frac{dE}{d\eta} \right|_{\eta=1} = 2T + V \quad (9)$$

with $T = T(1)$ and $V = V(1)$.

Now, we do not assume the fulfillment of any variational criterion for the wave function considered and do not require this derivative to vanish; instead, we shall determine it in a different manner, too.

We consider an infinitesimal compression with parameter $\eta = 1 + d\eta$. The vectors \vec{R}_α and \vec{P}_q change to \vec{R}_α/η and \vec{P}_q/η , respectively, which means that their differentials are $d\vec{R}_\alpha = -\vec{R}_\alpha d\eta$ and $d\vec{P}_q = -\vec{P}_q d\eta$ and their derivatives

$$\frac{d\vec{R}_\alpha}{d\eta} = -\vec{R}_\alpha; \quad \frac{d\vec{P}_q}{d\eta} = -\vec{P}_q \quad (10)$$

The scaling of the vectors \vec{r}_{iq} results in replacing the products $\zeta_j \vec{r}_{iq}$ with $\zeta_j(1 + d\eta) \vec{r}_{iq}$ which is equivalent to changing all the scaling factors ζ_j with $d\zeta_j = d\eta \zeta_j$, or

$$\frac{d\zeta_j}{d\eta} = \zeta_j \quad (11)$$

Then the full derivative of the energy according to η will be (we consider point $\eta = 1$):

$$\left. \frac{dE}{d\eta} \right|_{\eta=1} = \sum_\alpha \frac{\partial E}{\partial \vec{R}_\alpha} (-\vec{R}_\alpha) + \sum_q \frac{\partial E}{\partial \vec{P}_q} (-\vec{P}_q) + \sum_j \frac{\partial E}{\partial \zeta_j} \zeta_j \quad (12)$$

Comparing Eqs. (9) and (12) and bringing all terms to the same side, we get

$$2T + V + \sum_\alpha \vec{R}_\alpha \frac{\partial E}{\partial \vec{R}_\alpha} \Big|_{HF} + \sum_q \vec{P}_q \frac{\partial E}{\partial \vec{P}_q} - \sum_j \zeta_j \frac{\partial E}{\partial \zeta_j} = 0 \quad (13)$$

It is to be stressed that Eq. (13) is valid without assuming that the wave function has been subjected to any optimization. The first three terms are the ‘physical’ ones in the sense that they are also present for an exact wave function, while the other two become zero if a complete optimization of the wave function has been made. The different known versions of the virial theorem can be obtained from expression Eq. (13) by requesting the wave function to fulfill some requirements.

First of all, we should mention that the derivative $\left. \frac{\partial E}{\partial \vec{R}_\alpha} \right|_{HF}$ on the left-hand-side of (13) represents the Hellmann–Feynman force, because only the electron–nuclear and the nuclear–nuclear energy terms of the Hamiltonian depend explicitly on the nuclear positions. This is indicated by the subscript ‘HF’. However, if the basis orbitals are centered on the nuclei and ‘orbital following’ is assumed, then the positions of the basis orbitals move together with the nuclei and the sum of the first two derivative terms gives the full gradient of the energy for a fixed functional form of the wave function (e.g., fixed orbital coefficients), and we have

$$2T + V + \sum_\alpha \vec{R}_\alpha \frac{\partial E}{\partial \vec{R}_\alpha} \Big|_C - \sum_j \zeta_j \frac{\partial E}{\partial \zeta_j} = 0 \quad (14)$$

where $\left. \frac{\partial E}{\partial \vec{R}_\alpha} \right|_C$ is now pertinent to the total energy as function of the atomic positions \vec{R}_α and subscript ‘C’ indicates that we assume fixed wave function parameters (orbital coefficients etc.). The same result is obtained if the position of every basis orbital is optimized and all $\frac{\partial E}{\partial \vec{P}_q} = 0$. Of course, for a variational wave function the ‘true’ gradient of the energy coincides with the gradient of the energy for a fixed functional form of the wave function, as small variations of the latter do not change the variational energy and the subscript ‘C’ may be omitted.

It follows from (14) that the generally used variant of the virial theorem for the Born–Oppenheimer separation

$$2T + V + \sum_\alpha \vec{R}_\alpha \frac{\partial E}{\partial \vec{R}_\alpha} = 0 \quad (15)$$

is obtained assuming that we use a variational wave function and the scaling factors ζ_j were also optimized. Eq. (15) reduces to the simplest version of the virial theorem

$$2T + V = 0 \quad (16)$$

in the stationary points of the potential surface. This also means that the deviation from the equality $2T + V = 0$ in stationary points measures the degree to which the basis exponents are lacking optimization (if we are dealing with classical basis set expansions, like in the HFR method, then this deviation can be considered also as measuring the incompleteness of the basis set, as an optimized expansion in a complete basis does not need exponent optimization).

3. Examples

3.1. An example of a H atom with an off-centered Slater orbital

Let us consider a proton at the origin (for simplicity) and an electron occupying a Slater 1s orbital with exponent α at the distance R . According to the formulae in Slater’s book [10], one has (taking into account that Slater used Rydberg units instead of Hartrees, which means that all his results should be divided by two if we want to use Hartrees):

$$T = \frac{\alpha^2}{2} \quad (17)$$

and

$$V = \alpha \left[-\frac{1}{w} + e^{-2w} \left(1 + \frac{1}{w} \right) \right] = -\frac{1}{R} + e^{-2\alpha R} \left(\alpha + \frac{1}{R} \right) \quad (18)$$

where the definition $w = \alpha R$ has been taken into account. Comparing with the notations used above, we have the correspondence $R_\alpha = 0$, $P_q = R$ and $\zeta_j = \alpha$ – in this simple problem there is no need to explicitly consider vector variables.

According to Eqs. (17), (18), we have for the derivatives of $E = T + V$ the expressions

$$\frac{\partial E}{\partial R} = \frac{1}{R^2} - 2\alpha e^{-2\alpha R} \left(\alpha + \frac{1}{R} \right) - \frac{e^{-2\alpha R}}{R^2} \quad (19)$$

and

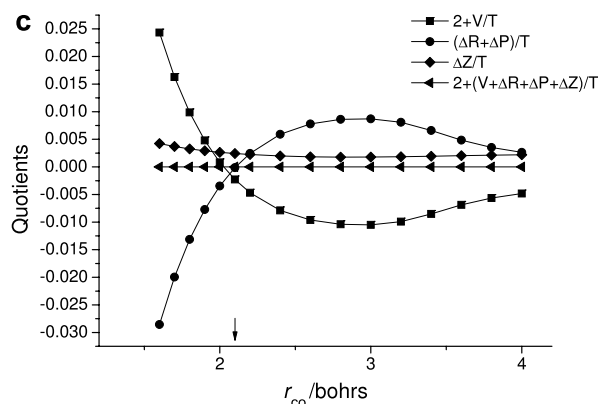
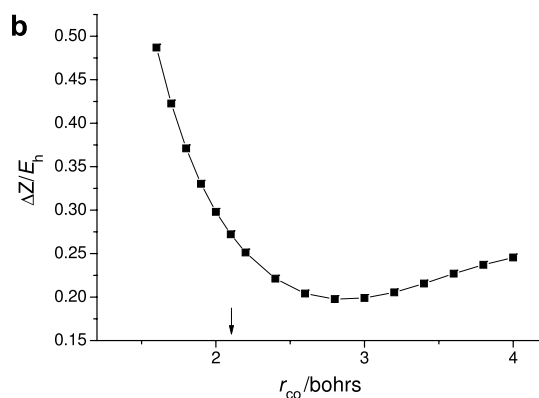
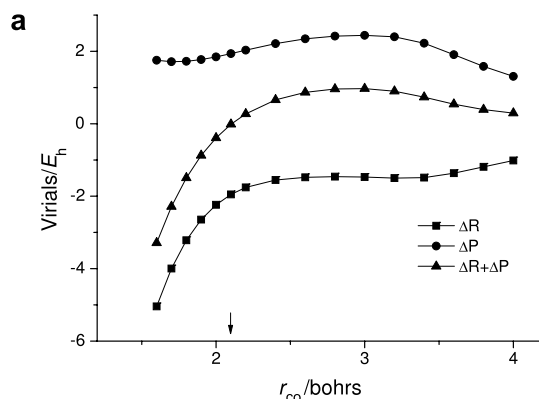


Fig. 1. (a) The quantities ΔR , ΔP defined in Eq. (22) and their sum as functions of the interatomic distance of the CO molecule (6-31G* HFR calculations); (b) the quantity ΔZ defined in Eq. (22) as function of the interatomic distance of the CO molecule; (c) the different contributions at the left-hand-side of Eq. (23) and their sum as functions of the interatomic distance of the CO molecule.

$$\frac{\partial E}{\partial \alpha} = \alpha - 2R e^{-2\alpha R} \left(\alpha + \frac{1}{R} \right) + e^{-2\alpha R} \quad (20)$$

Thus we have

$$\begin{aligned} 2T + V + R \frac{\partial E}{\partial R} - \alpha \frac{\partial E}{\partial \alpha} &= \alpha^2 - \frac{1}{R} + e^{-2\alpha R} \left(\alpha + \frac{1}{R} \right) \\ &+ \frac{1}{R} - 2R\alpha e^{-2\alpha R} \left(\alpha + \frac{1}{R} \right) - \frac{e^{-2\alpha R}}{R} - \alpha^2 \\ &+ 2\alpha R e^{-2\alpha R} \left(\alpha + \frac{1}{R} \right) - \alpha e^{-2\alpha R} = 0 \end{aligned} \quad (21)$$

in full agreement with Eq. (13)

3.2. LCAO model calculations

Dividing Eq. (13) by T and introducing the shorthand notations

$$\Delta R = \sum_{\alpha} \tilde{R}_{\alpha} \frac{\partial E}{\partial \tilde{R}_{\alpha}} \Big|_{HF}; \quad \Delta P = \sum_q \tilde{P}_q \frac{\partial E}{\partial \tilde{P}_q}; \quad \Delta Z = - \sum_j \zeta_j \frac{\partial E}{\partial \zeta_j} \quad (22)$$

it can be rewritten as

$$2 + (V + \Delta R + \Delta P + \Delta Z)/T = 0 \quad (23)$$

Eq. (23) indicates that the quantity $(\Delta R + \Delta P + \Delta Z)/T$ measures the deviation of the ratio V/T from its 'classical' value of $V/T = -2$.

We are going here to show some HFR results for two simple molecules, CO and NH_3 treated by using the standard 6-31G* basis set. For CO we have studied the behaviour of different quantities along the potential curve, while for NH_3 the inversion of the molecule has been considered by keeping fixed the N–H distances. The derivations with respect of centers and exponents of basis functions have been performed by using the technique developed in Ref. [4].

Fig. 1 collects different results for the CO molecule. Fig. 1a shows that for the given selection of the origin (the carbon nucleus) the components of the virial ΔR and

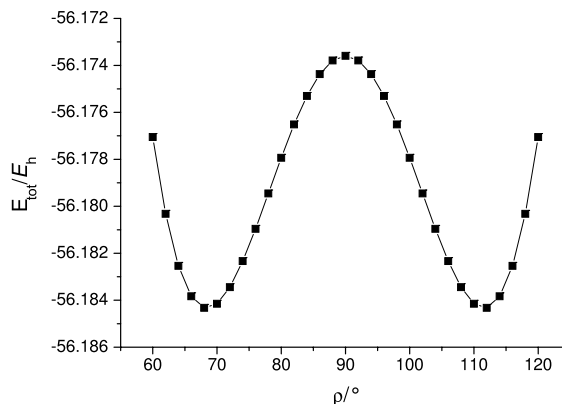


Fig. 2. Potential curve of the NH_3 molecule along the inversion coordinate using fixed N–H distances (6-31G* HFR calculations).

ΔP are of opposite sign; their sum crosses the zero level exactly at the equilibrium distance of 2.1047 bohr indicated by an arrow on the ordinate axis, as in this case this sum is the virial of the conventional gradient (this is also reflected on the respective curve on Fig. 1c.). The quantity ΔZ , shown on Fig. 1b, changes smoothly with the interatomic

distance, exhibiting a minimum at a distance significantly larger than the equilibrium one.

Fig. 1c displays the different terms contributing to the left-hand-side of Eq. (23), and the sum of all the terms at the left-hand-side, which was always found to equal zero with the full machine accuracy (ca. 14 decimal digits) at all distances. One can see that at the equilibrium distance, where $\Delta R + \Delta P = 0$, the deviation of the actual value $T/V = -2.00241$ from the ideal value of -2 is just due to the term ΔZ .

Fig. 2 displays the potential curve of the NH_3 molecule along the inversion coordinate (angle between the three-fold axis and the N–H bonds) at a fixed value of 1 Å of the N–H distances. It exhibits a maximum at the planar conformation ($\rho = 90^\circ$), and two minima at the angles $\rho = 68.42^\circ$ and 111.58° . As the bond lengths have not been optimized, the forces are not zero and their virial need not to vanish even at the stationary point of this potential curve.

Fig. 3 displays the same quantities for NH_3 as shown on Fig. 1 for CO (the positions of the energy minima are again indicated by arrows on the ordinate axis). As the origin has been kept on one side from the molecule throughout the calculations (on the three-fold axis, at a distance of 1 Å from the nitrogen atom), the curves of the origin-dependent quantities ΔR and ΔP are not symmetric with respect of the planar geometry; their sum, representing the virial of the true gradient is, of course, origin-independent and symmetric. The curve ΔZ (Fig. 2b) is symmetric and exhibits a maximum at the planar configuration.

Fig. 3c displays the different terms at the left-hand-side of Eq. (23) for the NH_3 molecule. Contrary to the CO case discussed above, the contribution coming from the total gradient does not vanish even at the minima or at the maximum of the energy curve: as the bond lengths have not been optimized, these points are not true stationary points of the whole potential surface. The sum of all terms of Eq. (23) again has been found zero with the full machine accuracy.

4. Conclusions

An extension of the virial theorem in the Born–Oppenheimer framework is presented, which is valid for arbitrary (not necessarily variational) wave functions built up by using finite local one-electron basis sets. It permits to define explicitly the terms causing deviations from the ‘ideal’ virial ratio; the standard formulations of the virial theorem can also be obtained from it as special cases. The results are illustrated by an analytical and some numerical examples.

Acknowledgements

I.M. expresses his gratitude to András T. Rokob and Dr. Andrea Hamza for the useful discussions.

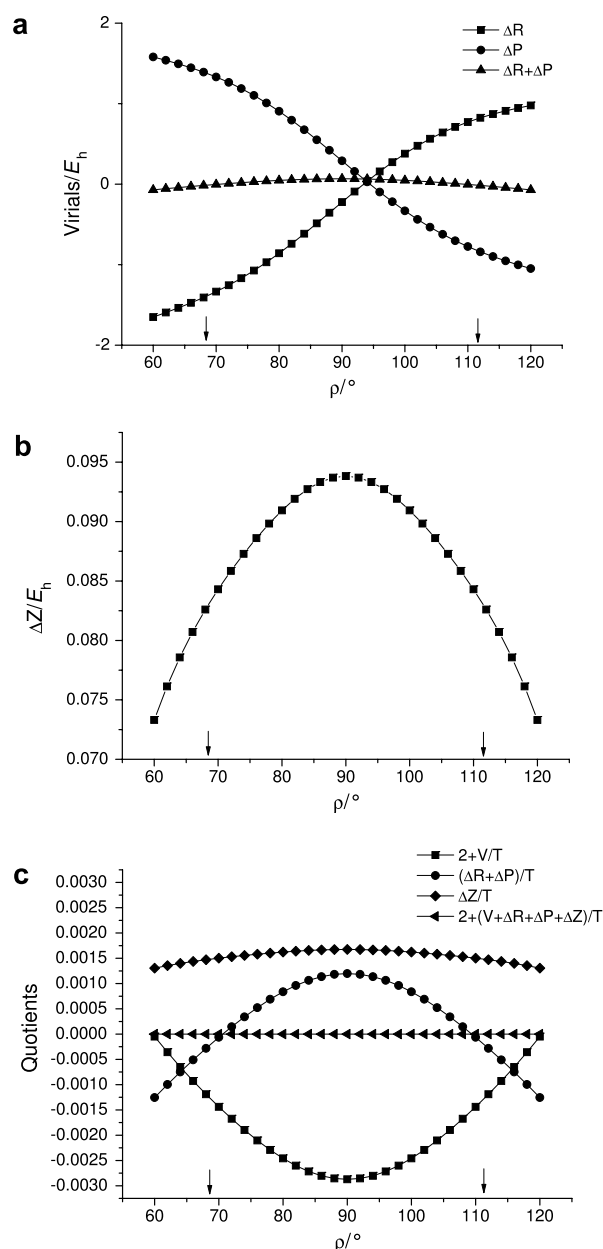


Fig. 3. (a) The quantities ΔR , ΔP defined in Eq. (22) and their sum as functions of the inversion coordinate of the NH_3 molecule (6-31G* HFR calculations); (b) the quantity ΔZ defined in Eq. (22) as function of the inversion coordinate of the NH_3 molecule; (c) the different contributions at the left-hand-side of Eq. (23) and their sum as functions of the inversion coordinate of the NH_3 molecule.

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