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Relativistic virial theorem for diatomic molecules. Application to H_2^+*

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Summary. The virial theorem for a molecule in the relativistic clamped-nuclei approximation is derived. The individual energy contributions A (momentum energy), B (mass energy), $T = A + B$ (kinetic energy) and V (potential energy) are expressed in terms of E, $\partial E/\partial R$ (derivative w.r.t. the nuclear coordinates) and the relativistic correction $\partial E/\partial \alpha^2$ (derivative w.r.t Sommerfeld's fine-structure constant α). If E and $\partial E/\partial R$ are known as functions of α, then all individual energy terms are also known as functions of α. As an example, numerical results for H_2^+ are presented. The relativistic and nonrelativistic potential energy curves and the paradoxical behavior of their different contributions are analyzed and interpreted in both the large R and short R ranges.

Key words: Diatomic molecules – Virial theorem – Hydrogen – Relativistic effects

1 Introduction

The virial theorem [1] is a very useful tool to acquire a deeper understanding of the behavior of physical systems. A very simple example is the nonrelativistic atom [2]. This case has early been extended to nonrelativistic molecules [see e.g. 3, 4] and to relativistic atoms [see e.g. 2, 5, 6]. Here we will investigate the case of relativistic molecules.

In nonrelativistic quantum mechanics, the total energy consists of two terms, the kinetic energy T, and the potential energy V, which both can, with the help of the virial relation, be obtained from the total energy alone (and from its derivative with respect to the internucelar distance in the case of a molecule). In relativistic quantum mechanics, however, there are three energy terms (the mass energy B, the momentum energy A, and the potential energy V), and so far no relation was known to obtain them individually from the total energy.

In Sect. 2 we will derive such relations between the relativistic molecular energy contributions, and the total energy and its derivatives. These relations are obtained

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* Dedicated to Professor W. Kutzelnigg on the occasion of his 60th birthday

by scaling techniques analogous to the ones used for the nonrelativistic virial theorem. In Sect. 3 we investigate the virial relation for the case of the H_2^+-molecule on the basis of accurate numerical calculations. They were performed with the help of the relativistic double perturbation theories of Rutkowski and Schwarz [7, 8], using the form of this approach as proposed by Kutzelnigg [9] under the name "direct perturbation theory". Our results are summarized in Sect. 4.

2 Theory

We assume that the Hamiltonian may be written as:

$$\hat{H}_R(r) = \hat{B} + \hat{A}(p) + \hat{V}_R(r), \tag{1}$$

where for a Dirac one-electron diatomic molecule:

$$\hat{B} = \hat{\beta}' m c^2 \quad \text{with} \quad \hat{\beta}' = \hat{\beta} - 1, \tag{2a}$$

$$\hat{A} = \hat{\alpha} \cdot \hat{p} c, \tag{2b}$$

$$\hat{V} = Z_1 Z_2 / R_{12} - (Z_1 / |R_1 - r| + Z_2 / |R_2 - r|). \tag{2c}$$

Here we use atomic units ($m = e = \hbar = 1$, so $c = 1/\alpha$; however we still keep m in the equations) and the other symbols have their standard meaning. R and r are the nuclear and electronic coordinates, respectively. In the clamped-nuclei approximation:

$$\hat{H}_R(r) \cdot \Psi_R(r) = \Psi_R(r) \cdot E_R. \tag{3}$$

where

$$E_R = \langle \Psi_R | \hat{H}_R | \Psi_R \rangle_r \quad \text{with} \quad \Psi_R = \begin{bmatrix} \Psi_+ \\ \Psi_- \end{bmatrix} \tag{4}$$

may be split up into the following contributions ε_R:

$$E = T + V, \tag{4a}$$

$$T = A + B, \tag{4b}$$

$$V = V_+ + V_-. \tag{4c}$$

Here we have omitted the subscript R for convenience. The individual energy contributions ε are given by:

$$A = \langle \Psi | \hat{A} | \Psi \rangle = 2 \mathrm{Re} \langle \Psi_+ | \hat{\sigma} \cdot \hat{p} c | \Psi_- \rangle, \tag{5a}$$

$$B = \langle \Psi | \hat{B} | \Psi \rangle = -2 m c^2 \langle \Psi_- | \Psi_- \rangle = -2 m c^2 S_-, \tag{5b}$$

$$V_\pm = \langle \Psi_\pm | \hat{V} | \Psi_\pm \rangle, \; S_\pm = \langle \Psi_\pm | \Psi_\pm \rangle. \tag{5c}$$

i.e. $S_- + S_+ = 1$. In the nonrelativistic limit, $c^{-1} = \alpha \to 0$, we obtain with $\Psi_{0-} = \dfrac{\hat{\sigma} \cdot \hat{p}}{2mc} \Psi_{0+}$:

$$E_0 = T_0 + V_0, \tag{6a}$$

$$T_0 = A_0 + B_0 = \tfrac{1}{2} A_0 = -B_0 = \langle \Psi_{0+} | \hat{p}^2 / 2m | \Psi_{0+} \rangle, \text{ i.e. } A_0 + 2B_0 = 0, \tag{6b}$$

$$V_0 = V_{0+}, \; S_+ = 1 \quad \text{and} \quad V_{0-} = 0, \; S_- = 0. \tag{6c}$$

Introducing the dilatation generator [6]:

$$\hat{G} = r \cdot \frac{\partial}{\partial r} + R \cdot \frac{\partial}{\partial R}, \tag{7}$$

we find that, for an eigenfunction $\Psi_R(r)$ of $\hat{H}_R(r)$:

$$\langle \Psi_R | [\hat{G}, \hat{H}] | \Psi_R \rangle = R \cdot \frac{dE}{dR} = R \cdot E'. \tag{8}$$

Since for Coulombic potentials:

$$[\hat{G}, \hat{H}] = -\hat{A} - \hat{V}, \tag{9}$$

we obtain the *relativistic diatomic virial theorem* in the following equivalent forms:

$$\boxed{\begin{aligned} A &= -V - R \cdot E' \\ &= -2E - 2R \cdot E' + (A + 2B), && (10a) \\ B &= E + R \cdot E', && (10b) \\ T &= -E - R \cdot E' + (A + 2B), && (10c) \\ V &= 2E + R \cdot E' - (A + 2B). && (10d) \end{aligned}}$$

This yields (see Eq. (6b)) the well-known nonrelativistic limit:

$$T_0 = A_0/2 = -B_0 = -E_0 - R \cdot E_0', \tag{11a}$$

$$V_0 = 2E_0 + R \cdot E_0'. \tag{11b}$$

In the nonrelativistic case, both energy contributions T_0 and V_0, and also A_0, B_0, V_{0+}, V_{0-} are all uniquely determined by E_0 and E_0'. In the relativistic case, however, the single virial relation is not sufficient to obtain them individually from E and E' alone. Searching for an additional relation, we form the scalar product of $\langle \Psi_- |$ with the lower two lines of the Dirac equation (see Eqs. (1) and (2)), add the conjugate equation and obtain:

$$\boxed{A + 2B = -2V_- + 2S_- \cdot E = \{\langle \hat{B}\hat{V} \rangle - B \cdot E\}/mc^2 \propto O(\alpha^2).} \tag{12}$$

Still a term in addition to E and E' is needed, for instance $-2V_- = \langle \hat{B}\hat{V} \rangle / mc^2$, in order to obtain A, T, V individually.

Furthermore, in analogy to Eq. (7), we form the operator $\alpha^2 \frac{\partial}{\partial \alpha^2} = -\frac{1}{2} c \frac{\partial}{\partial c}$. Operating on the vanishing expectation value $\langle \Psi | -2(\hat{H} - E) | \Psi \rangle$, one obtains, according to the Hellmann–Feynman-theorem [20]:

$$\begin{aligned} 0 &= \alpha^2 \frac{\partial}{\partial \alpha^2} \langle \Psi | -2(\hat{H} - E) | \Psi \rangle \\ &= \left\langle \Psi \left| c \frac{\partial}{\partial c} (\hat{A} + \hat{B} + \hat{V} - E) \right| \Psi \right\rangle, \end{aligned} \tag{13a}$$

which yields (compare Eq. (3.12) of Ref. [18]):

$$0 = \left\langle \Psi \middle| \hat{A} + 2\hat{B} - c\frac{\partial E}{\partial c} \middle| \Psi \right\rangle, \tag{13b}$$

that is:

$$\boxed{A + 2B = -2\alpha^2 \cdot \frac{\partial E}{\partial \alpha^2}.} \tag{14a}$$

This is the relativistic generalization of Eq. (6b). Expanding Eq. (14a) in powers of α^2, one obtains for the n^{th} order:

$$\boxed{A_n + 2B_n = -2nE_n, \quad n = 0, 1, 2, \cdots .} \tag{14b}$$

In order to obtain the different energy contributions individually, one only needs E in the case of a nonrelativistic atom. One needs $\frac{\partial E}{\partial R}$ in addition in the case of a nonrelativistic molecule; and one needs $\frac{\partial E}{\partial \alpha^2}$ in addition in the relativistic cases. We can now express the energy contributions of a relativistic molecule as:

$$A = -2E - 2R \cdot \frac{\partial E}{\partial R} - 2\alpha^2 \cdot \frac{\partial E}{\partial \alpha^2}, \tag{15a}$$

$$B = E + R \cdot \frac{\partial E}{\partial R}, \tag{15b}$$

$$T = -E - R \cdot \frac{\partial E}{\partial R} - 2\alpha^2 \cdot \frac{\partial E}{\partial \alpha^2}, \tag{15c}$$

$$V = 2E + R \cdot \frac{\partial E}{\partial R} + 2\alpha^2 \cdot \frac{\partial E}{\partial \alpha^2}, \tag{15d}$$

The different relativistic orders A_n, B_n, T_n and V_n can individually be expressed by E_n and $E_n' = \partial E_n / \partial R$:

$$A_n = -(2 + 2n)\, E_n - 2RE_n', \tag{16a}$$

$$B_n = E_n + RE_n', \tag{16b}$$

$$T_n = -(1 + 2n)\, E_n - RE_n', \tag{16c}$$

$$V_n = (2 + 2n)\, E_n + RE_n'. \tag{16d}$$

Equations (16) show that the partial cancellation of T and V becomes more and more pronounced for higher relativistic orders. To obtain V_{-n} and

$V_{+n} = V_n - V_{-n}$, E_i and E_i' are needed not only for $i = n$ but also for $i < n$:

$$V_{-n} = n \cdot E_n - \tfrac{1}{2} \sum_{i=1}^{n} E_{n-i} \cdot (E_{i-1} + RE'_{i-1}). \tag{16e}$$

3 Application to H_2^+

The energy contributions of H_2^+ as a function of $\ln R$ have been accurately calculated numerically at 20 R-values using our relativistic perturbation approach [8]. They are shown in Fig. 1a. For such a light molecule, the curves are indistinguishable from the nonrelativistic ones. Therefore the first- and second-order relativistic corrections of order α^2 and α^4, resp., are shown separately in Figs. 1b, c.

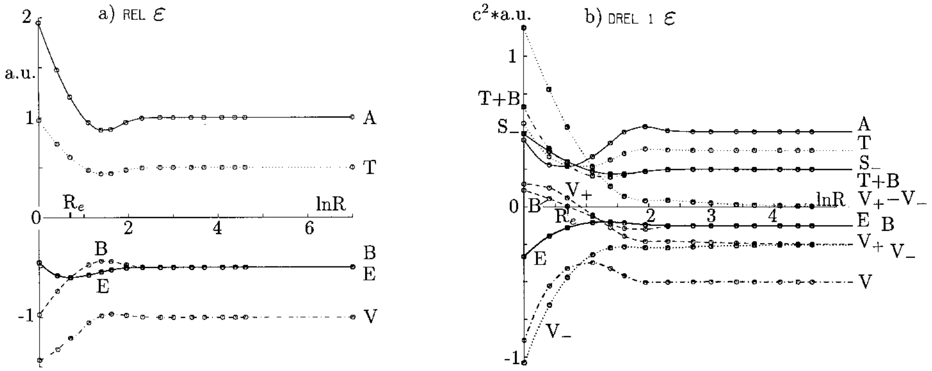
3.1 Separated atoms

At $R \to \infty$, where $R \cdot E' = 0$ (for H + H^+ e.g.), we obtain:

$$A = -2(E + \mathrm{d}E/\mathrm{d}\ln\alpha^2) \approx -2E_0 - 4E_1, \tag{17a}$$

$$B = E, \tag{17b}$$

$$V = -A. \tag{17c}$$



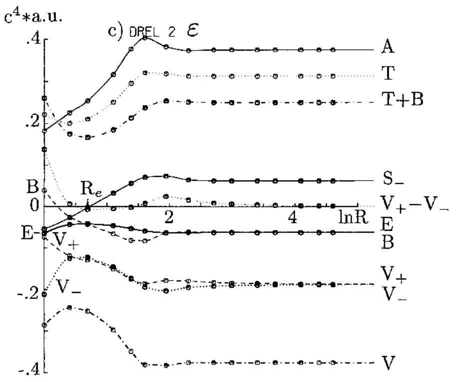


Fig. 1a–c. Total energy E and individual energy contributions ε of H_2^+ versus $\ln R$ (R = internuclear distance in a.u.). Equilibrium distance is $R_e \approx 2$ a.u. ($\ln R = 0.69$).
a) REL is the relativistic energy in a.u., which is here indistinguishable from the zeroth order nonrelativistic contribution.
b) DREL1 is the first-order relativistic contribution $\sim \alpha^2$.
c) DREL2 is the second-order relativistic contribution $\sim \alpha^4$.
A: ——, B: – – –, $E = T + V$: ——, $S_- = \langle \Psi_- | \Psi_- \rangle$: ——, $T = A + B$: . . . . . , $A + 2B = T + B$: –·–·–, $V = V_+ + V_-$: ·—·—·, V_+: – – –, V_-: . . . . , $V_+ - V_-$: . . . .

In accordance with Eqs. (10, 12, 14, 16) and (17), the analytical 1*s*-eigensolution of the hydrogen atom [10] yields (compare e.g. [21]):

$$\begin{aligned} A = -V &= 1 + \tfrac{1}{2}\alpha^2 + \tfrac{3}{8}\alpha^4 + \cdots, && (18a)\\ B = E &= -\tfrac{1}{2} - \tfrac{1}{8}\alpha^2 - \tfrac{1}{16}\alpha^4 + \cdots, && (18b)\\ T = A + B &= \tfrac{1}{2} + \tfrac{3}{8}\alpha^2 + \tfrac{5}{16}\alpha^4 + \cdots, && (18c)\\ A + 2B &= \tfrac{1}{4}\alpha^2 + \tfrac{1}{4}\alpha^4 + \cdots, && (18d)\\ V_+ &= -1 - \tfrac{1}{4}\alpha^2 - \tfrac{3}{16}\alpha^4 + \cdots, && (18e)\\ V_- &= -\tfrac{1}{4}\alpha^2 - \tfrac{3}{16}\alpha^4 + \cdots, && (18f)\\ V_+ - V_- &= -1, && (18g)\\ S_- &= \tfrac{1}{4}\alpha^2 + \tfrac{1}{16}\alpha^4 + \cdots. && (18h) \end{aligned}$$

All these expansions converge better than $\Sigma(Z\alpha)^2$ for a hydrogenic atom with nuclear charge Z. In the relativistic case, $A + 2B = A + 2E = T + B$ deviates from 0 by an order of α^2. For Coulombic systems this deviation is positive in any order because of Eqs. (14). The factors in Eqs. (18) in front of $\alpha^0, \alpha^2, \alpha^4$ are the limiting values for large R in Figs. 1a, b, c, respectively. From Eqs. (17, 18) follows:

$$\begin{aligned} T/-E &= 1 + \tfrac{1}{2}\alpha^2 + \tfrac{3}{8}\alpha^4 + \cdots \approx 1 + 2E_1/E_0 > 1 = T_0/-E_0, && (19a)\\ V/E &= 2 + \tfrac{1}{2}\alpha^2 + \tfrac{3}{8}\alpha^4 + \cdots \approx 2 + 2E_1/E_0 > 2 = V_0/E_0, && (19b)\\ -V/T &= 2 - \tfrac{1}{2}\alpha^2 - \tfrac{1}{8}\alpha^4 - \cdots \approx 2 - 2E_1/E_0 < 2 = -V_0/T_0. && (19c) \end{aligned}$$

For nonrelativistic atoms:

$$2T_0 = A_0 = -V_0 = -2B_0 = -2E_0, \tag{20}$$

whereas for relativistic atoms (first order expressions are given in parentheses underneath, $\varepsilon = |E_0|$ and $\delta = |E_1|$):

$$\begin{matrix} 2T & > & A = -V & > & -2B = -2E. \\ (2\varepsilon + 6\delta) & & (2\varepsilon + 4\delta) & & (2\varepsilon + 2\delta) \end{matrix} \tag{21a}$$

This holds for total energies (compare the numerical data of Desclaux [11]). Concerning *orbital energies* we observe that (compare Schwarz et al. [12]), except for the innermost shells (K, L), where $-V > -2E > T > -E$:

$$2T > A > -V \gtrsim T > -2E, \tag{21b}$$

see Table 1 for the U atom (the other atoms behave similarly). Note that potentials like the Hartree–Fock one decrease faster towards the nucleus than the Coulomb potential, $\sim r^{-1}$, because of significant screening by the core electrons far from the nucleus. In this case $r \cdot \partial\hat{V}/\partial r > -\hat{V}$ so that $A > -V$ holds in general for orbitals.

The hydrogenic Schrödinger Hamiltonian and its lowest order relativistic correction read:

$$\begin{aligned} \hat{H} &= \hat{H}_0 + \hat{H}_1 + \cdots, && (22)\\ \hat{H}_0 &= \hat{T}_0 + \hat{V}_0 = p^2/2m - Z/r, && (22a)\\ \hat{H}_1 &= \hat{T}_1 + \hat{V}_1 = -p^4\alpha^2/8m^3 + Z\alpha^2/2m^2 \cdot (\pi \cdot \delta(r) + 1/r^3 \cdot \mathfrak{l} \cdot \mathfrak{s}). && (22b) \end{aligned}$$

The first-order "direct" relativistic correction energies for the H-atom are:

$$\Delta_1^d T = \langle \Psi_0 | \hat{T}_1 | \Psi_0 \rangle = -\tfrac{5}{8}\alpha^2, \tag{23a}$$

Table 1. Orbital energy contributions (in a.u.) for the U atom. (Where the order of values deviates from the one given in the headline, it is noted explicitly)

Orbital	$2T$	>	$-V$	>	T	>	$-2E$
$1s$	12818		10688		6409	<	8558
$2s$	3192		2402		1596	<	1612
$2p1/2$	3177		2365		1588		1553
$2p3/2$	2021		1646		1011	<	1271
$3s$	1021		717		511		413
$3p1/2$	1006		696		503		386
$3p3/2$	716		518		358		321
$3d3/2$	699		489		350		278
$3d5/2$	645		455		323		265
⋮							
$5f5/2$	22.7		11.7		11.3		0.694
$5f7/2$	21.5		11.1		10.8		0.639
$6d3/2$	4.75		2.57		2.37		0.386
$6d5/2$	4.19		2.28		2.10		0.367
$7s$	2.53		1.47		1.27		0.405

which is negative, and:

$$\Delta_1^d V = \langle \Psi_0 | \hat{V}_1 | \Psi_0 \rangle = +\tfrac{1}{2}\alpha^2, \tag{23b}$$

which is positive. However, because of the "indirect" contributions due to relativistic orbital relaxation:

$$\Delta_1^i T = \langle \Psi_1 | \hat{T}_0 | \Psi_0 \rangle + \langle \Psi_0 | \hat{T}_0 | \Psi_1 \rangle = +\alpha^2, \tag{24a}$$

$$\Delta_1^i V = \langle \Psi_1 | \hat{V}_0 | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}_0 | \Psi_1 \rangle = -\alpha^2, \tag{24b}$$

the total relativistic first-order corrections are of opposite sign to the direct ones, namely $\Delta_1 T = +3/8\alpha^2$ and $\Delta_1 V = -1/2\,\alpha^2$, as given in Eq. (18). Compare the discussion in Sect. 2.4 of Ref. [18].

3.2 Recapitulation: Nonrelativistic limit of the molecule

3.2.1 Very large distances ($R > 20$, $\ln R > 3$). The dominant interaction is the dipole polarization of a H-atom by a proton, i.e. $E = E(H) - \frac{a}{2}R^{-4}$, where a is the dipole polarizability of H. In the following, changes of expectation value ε due to bond formation will be denoted by $B\varepsilon = \varepsilon(R) - \varepsilon(\infty)$, i.e. $BE = -\frac{a}{2}R^{-4}$. From the virial relations of Eqs. (16) we obtain for the different bond energy contributions:

$$BA_0/BE_0 = +6, \tag{25a}$$

$$BB_0/BE_0 = -3, \tag{25b}$$

$$BT_0/BE_0 = +3, \tag{25c}$$

$$BV_0/BE_0 = -2. \tag{25d}$$

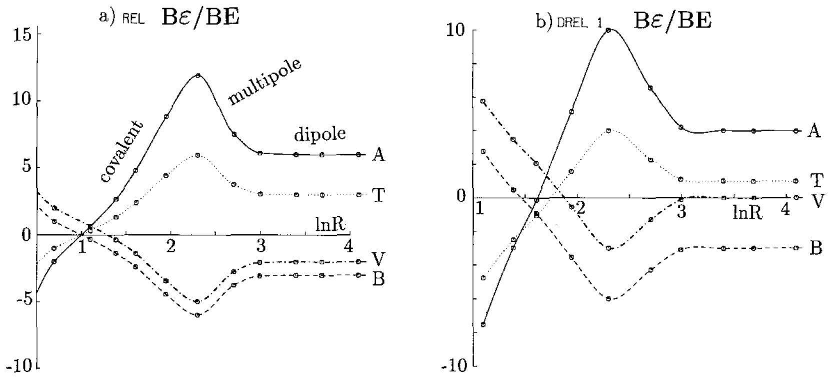


Fig. 2a, b. Bond energy contributions $B\varepsilon = \varepsilon(R) - \varepsilon(\infty)$ from A, B, T and V, *divided* by the total bond energy, $BE = E(R) - E(\infty)$. See legend of Fig. 1. Since BE_0 is negative, an increase of the curves in **Fig. 2a** means a decrease of the individual contributions. However, BE_1 is positive in the R-range of **Fig. 2b**

For decreasing R, A_0, T_0 and E_0 decrease while B_0 and V_0 increase. Note that, according to Eq. (11), E_0 and B_0 vary for large R in opposite directions for any $E_0 \sim -R^{-n}$ with $n > 1$ (and V_0 increases for $n > 2$), and that polarization increases V. Polarization distorts the hydrogen atom towards the proton so that the electron is, on the average, more distant from its "own" attracting nucleus. The spatial region available for the electron thereby becomes larger, corresponding to an even larger T-decrease (Heisenberg's uncertainty relation). That is, the energetic stabilization due to polarization is caused by kinetic energy lowering, partially compensated by potential energy increase. This paradox at large R is similar to the one of covalent bond formation at R_e and had already been elucidated by Ruedenberg [14] and Kutzelnigg [15].

While the first order polarized wavefunction is already sufficient to obtain the correct polarizability and polarization energy BE [17], the second-order wavefunction is needed to obtain the correct polarization effects on the individual energy contributions, i.e. the ratios of Eq. (25). The long-range energy changes are too small to be visible in Fig. 1. Therefore we have plotted $B\varepsilon/BE$ explicitly in Fig. 2. The values of Eqs. (25) are the limiting values for large R in Fig. 2a.

3.2.2 Medium large distances ($10 < R < 20$, $\ln R \in [2.3, 3]$). Hyperpolarization effects become important. For $BE \sim R^{-6}$, for instance, one obtains from the virial relations:

$$BA/BE = 10, \tag{26a}$$

$$BB/BE = -5, \tag{26b}$$

$$BT/BE = 5, \tag{26c}$$

$$BV/BE = -4. \tag{26d}$$

These values are obtained near $R = 12$ ($\ln R = 2.5$), see Fig. 2a.

3.2.3 Intermediate distances ($4 < R < 10$, $\ln R \in [1.4, 2.3]$). The kinetic energy $T_0 = \frac{1}{2}A_0 = -B_0$ decreases further (see Fig. 1a, enlarged in Fig. 3a) with decreasing

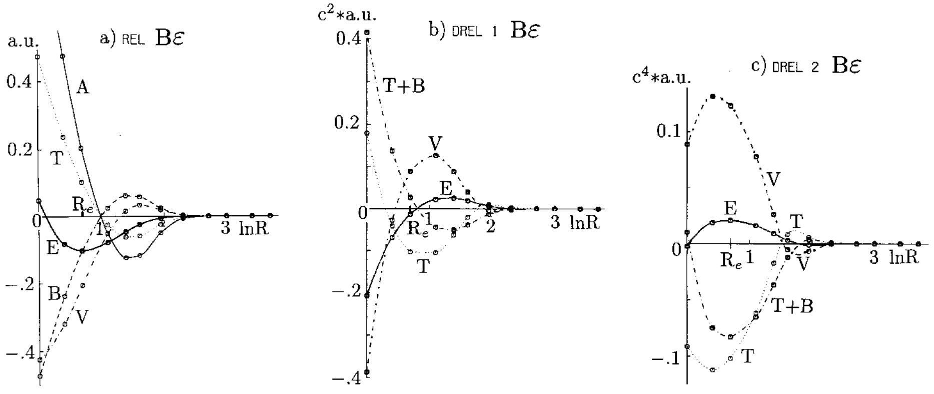


Fig. 3a–c. Bond energy contributions $B\varepsilon$ versus $\ln R$, see legend of Fig. 1

R because of the beginning of the formation of the covalent bond by quantum mechanical interference, i.e. by electron sharing of the atomic valence electron between the two atoms (Δx increase and Δp decrease according to Heisenberg's uncertainty principle, see [13–15]). Simultaneously, down to $R \sim 5$ a.u., the electron density accumulates in the overlap region around the bond center, reducing the density near the nuclei so that V (and B) also increase furthermore (i.e. decrease in value). Accordingly all energy contributions, if divided by V or T, vary less.

3.2.4 Distances around R_e. For decreasing R-values the electron density distribution now begins to contract towards the nuclei [14], so that finally V drops below its asymptotic atomic value, and T increases above its asymptotic value (see Fig. 3a). At the equilibrium internuclear separation, B and E become equal again. At shorter distances, the total energy starts to increase, corresponding to the fact that the electronic potential energy decrease becomes more and more compensated by the internuclear repulsion.

The behavior of A, B, T, V and E around R_e is enlarged in Fig. 4a. Expanding the energy in a Taylor series around R_e with $x = R - R_e$,

$$E = E_e + k\frac{x^2}{2} - b\frac{x^3}{6} + \cdots, \tag{27a}$$

we obtain, omitting the index $_0$ for the nonrelativistic case,

$$-A/2 = -T = B = E_e + kR_e x + (3k - bR_e)\frac{x^2}{2} - \cdots \tag{27b}$$

$$V = 2E_e + kR_e x + (4k - bR_e)\frac{x^2}{2} - \cdots, \tag{27c}$$

i.e. V, B, $-T$ and $A/2$ have the same slope $k \cdot R_e$ at R_e. Note that there are two contributions to terms like kx^2 etc., one from E and the other one from $R \cdot E' = (R_e + x) \cdot E'$.

3.3 Relativistic corrections to the molecular potential curve

The zeroth-order contributions to $\hat{A}$, $-\hat{B}$, $\hat{T}$ correspond to $+p^2$. They are positive. For decreasing R, they decrease at first, and then increase strongly for $R < 4$ ($\ln R < 1.3$) (see Figs. 1a, 3a), as explained above. The relativistic first-order contributions correspond to $-p^4$ ($\hat{T}_1 \sim -\hat{T}_0^2/2mc^2$). So one might expect that $A_1, T_1, -B_1$ are negative and increase at first and then decrease. However, $A_1, T_1, -B_1$ are positive at large R (see Sect. 3.1 and Figs. 1b, 2b), and they exhibit a more complicated behavior at shorter R (see also Fig. 3b), due to the interplay of "direct" and "indirect" contributions mentioned in Sect. 3.2.

3.3.1 Large-R dipole-interaction range ($R > 20$, $\ln R > 3$). The relativistic bond energy changes are due to the relativistic changes of the dipole polarizability, the lowest orders of which are (see e.g. [16]):

$$a_0 = 4.5, \qquad a_1 = -\tfrac{14}{3}\alpha^2, \qquad a_2 = 0.1175\ldots\alpha^4. \tag{28}$$

The relativistic reduction of the polarizability ($a_1 < 0$) reduces the value of the (negative) binding energy, $BE_1 = +7\alpha^2/3R^4$. Concerning the individual contributions, it follows from the virial relations of Eqs. (16) that:

$$BA_n/BE_n = +6 - 2n, \tag{29a}$$

$$BB_n/BE_n = -3, \tag{29b}$$

$$BT_n/BE_n = +3 - 2n, \tag{29c}$$

$$BV_n/BE_n = -2 + 2n. \tag{29d}$$

The $n = 1$ first-order ratios are the values for large R in Fig. 2b. Since a_1 is negative, E_1 and T_1 increase, and B_1 decreases at first for decreasing R. For large R, $\hat{T}$ determines the sign of the bond energy: BT_0 and BE_0 are both negative (bonding), BT_1 and BE_1 are both positive (antibonding relativistic correction). This is as expected above.

3.3.2 Intermediate R values. T_0 and V_0 (Fig. 3a) change their trends around $R \approx 4$ to 5. At shorter R-values T_0 increases and V_0 decreases, due to the beginning of orbital contraction, and they reach their asymptotic values again. T_1 and V_1 (Fig. 3b), however, already change their trends around $R \approx 6$. For distances down to $R \approx 3$, T_1 decreases (bonding), and V_1 increases even more so that E_1 remains antibonding. The relativistic correction to the virial relation, $B(A + 2B)$, is negative in this R-range. The second order corrections (Fig. 3c) are comparatively small.

3.3.3 Distances around R_e (see Figs. 2 and 4). $T_0 \approx \frac{1}{2}A_0$ increases and $V_0 \approx B_0$ decreases for decreasing R, so that E_0 becomes stationary at the negative value BE_0, because the dominating contribution V_0 is negative. Because V_1 decreases more strongly with decreasing R than T_1 increases, E_1 decreases; accordingly a relativistic bond length contraction results. While V_{+1} and V_{-1} have the same value for the separated atoms, their contributions to the bond energy are opposite. From the virial relations one obtains for the slopes at R_e:

$$BA_1' = -3q_1 + 2k_1R_e, \tag{30a}$$

$$BB_1' = q_1 + k_1R_e, \tag{30b}$$

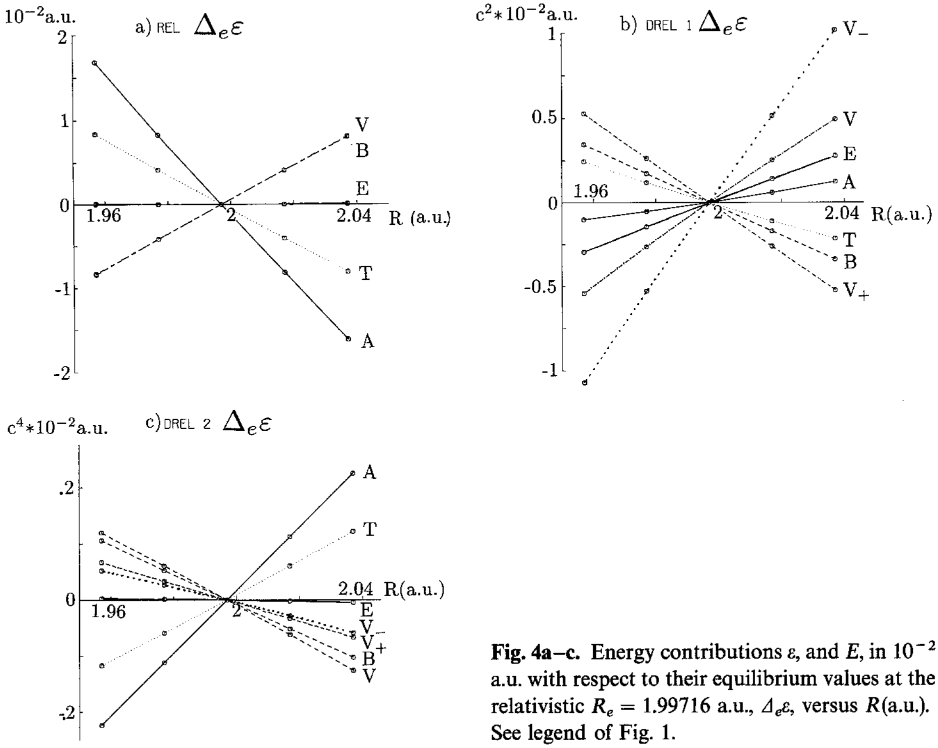


Fig. 4a–c. Energy contributions ε, and E, in 10^{-2} a.u. with respect to their equilibrium values at the relativistic $R_e = 1.99716$ a.u., $\Delta_e\varepsilon$, versus R(a.u.). See legend of Fig. 1.

$$BT_1' = -2q_1 - k_1 R_e, \tag{30c}$$

$$BV_1' = 2.5 q_1 + k_1 R_e, \tag{30d}$$

$$BE_1' = 0.5 q_1, \tag{30e}$$

where $q_1 = E' - E_0'$ and $k_1 = E'' - E_0''$ at the relativistic R_e. Note that k_1 is not the complete relativistic change of the force constant, since the anharmonicity contribution due to the relativistic change of R_e is not included, see [8].

Second order relativistic bond energy corrections are shown in Fig. 4c. They are numerically rather small. While the atomic first- and second-order corrections are of the same sign (negative) for the atom, BE_1 changes sign near R_e and BE_2 is positive there.

Conclusion

We have derived the virial theorem for relativistic molecules with clamped nuclei. The particle interactions are assumed to be homogeneous in r^{-1}, i.e. comprizing the electrostatic Coulomb and magnetic Gaunt interactions. Then, due to relativity, the term $(A + 2B)$ has to be added (Eqs. (10)) to the nonrelativistic virial relations of Eq. (11). $(A + 2B)$ vanishes in the nonrelativistic limit. It can be expressed with the help of the lower component's contribution to the energy (Eq. (12)) or with the derivative of the energy with respect to α^2 (Eq. (14a)). All relativistic orders of $(A + 2B)$ can then be expressed by the respective orders of the total energy E (Eq. (14b)) so that each relativistic order of A, B, T and V can be expressed by the respective order of E and $\partial E/\partial R$ alone (Eqs. (16)). While the virial theorem for molecules contains $\partial E/\partial R$, the relativistic virial theorem also contains $\partial E/\partial\alpha^2$ (Eqs. (15)). We note that retardation of the electron–electron interaction will introduce small deviations from these relations.

Concerning the H_2^+ molecule, the relativistic change of the potential energy with R is negligible at very large R, while the relativistic correction of the kinetic energy is opposed to the binding behavior of the nonrelativistic kinetic energy, corresponding to the relation $\hat{T}_1 \sim -\hat{T}_0^2$. At medium distances, typical for covalent bonding, where V_0 decreases and T_0 increases, the relativistic correction to the bond energy changes from *bond-destabilizing* ($BE_1 > 0$) at larger R-values to *bond-stabilizing* at shorter R-values. Since $\mathrm{d}BE_1/\mathrm{d}R > 0$ *in this R-range*, the relativistic correction is *always bond-contracting.* Obviously, Gordy's rule [19], namely that bond stabilization goes proportional to bond contraction, will not hold for relativistic effects in general. It will hold only if R_e is below the critical value where BE_1 becomes negative. For H_2^+, which has a very short bond length, ($R_e = 2$), R_e is indeed smaller than $R_{\mathrm{crit}} = 2.25$. $\mathrm{d}BE_1/\mathrm{d}R$ is positive for medium R-values because $\mathrm{d}BV_1/\mathrm{d}R$ is so large. This may be rationalized as follows: While the direct relativistic contributions to V are antibonding and to T are bonding (Eq. (18b)) the synergetic bonding and relativistic *orbital contractions* decrease V and increase T. These rules hold for bonding due to $s\sigma$-interactions and for the special case where there are no core shells.

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