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Relativistic perturbation theory of molecular structure*

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Summary. The recently developed relativistic double perturbation theory is extended to handle relativistic changes of molecular structure more easily. This is achieved by simple coordinate scalings. Accurate higher order mixed perturbation energies for H_2^+ are calculated. The relativistic changes of bond energy, ΔDE, of bond length, ΔR_e, and especially of force constant, Δk, and of anharmonicity, Δa, are large, up to $100\% \cdot (Z/c)^2$. The dominant contributions to Δk and Δa are due to the "indirect" change of the nonrelativistic k and a connected with the relativistic change of bond length. Accordingly the relativistic changes obey Badger's and Gordy's rules ($-\Delta R \sim \Delta DE \sim \Delta k$).

Key words: Molecular structure – Relativistic perturbation theory

1 Introduction

The equlibrium structure $\boldsymbol{R}_e$ of a molecule with Born–Oppenheimer Hamiltonian $H_0(\boldsymbol{R})$ can be changed by a perturbation ΔH. ΔH may be an external field (such as a magnetic or electric laboratory field; or the electrostatic field above the surface of a solid, e.g. of an adsorbed molecule or of a molecule on the tip of a field desorption mass spectrometer; or the Madelung potential in a cavity of an ionic crystal surrounding a molecule or atom group; etc.). ΔH may also be a genuine term of the total Hamiltonian H, which has been neglected in the approximate Hamiltonian H_0 (such as electron correlation in the Hartree–Fock approximation; or relativity in the nonrelativistic approximation; etc.).

Double perturbation theory is a useful tool both to estimate and, especially, to elucidate the structural change $\Delta \boldsymbol{R}_e$ due to ΔH. Then the first perturbation is the change of the nuclear potential due to the shift $\Delta \boldsymbol{R}_e$ of the nuclear positions, and the second perturbation is $\Delta H(\boldsymbol{R})$ mentioned above. In the present paper, ΔH will be the relativistic correction. We write the total Hamiltonian as:

$$H = H_0(\pi \cdot \Delta \boldsymbol{R}_e) + \varrho \cdot \Delta H(\pi \cdot \Delta \boldsymbol{R}_e) = H_0(\delta \cdot \boldsymbol{R}_e^0) + \varrho \cdot \Delta H(\delta \cdot \boldsymbol{R}_e^0), \qquad (1)$$

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where the two formal perturbation parameters π and ϱ vary from 0 to 1. π monitors the potential from the nonrelativistic nuclear equilibrium position ($\pi \cdot \Delta R_e = 0$) to the relativistic one ($1 \cdot \Delta R_e$); ϱ monitors relativity from the nonrelativistic case ($\varrho = 0$, $c = \infty$) to the relativistic case ($H = H_0 + 1 \cdot \Delta H$). We expand the energy as a power series of the relativistic parameter ϱ, and of the structural change parameter δ with $\delta \cdot R = \pi \cdot \Delta R_e$ (we use δ instead of π, so we need not know the ΔR_e in advance):

$$E(\delta, \varrho) = \sum_{p,r} E^{(p,r)} \cdot \delta^p \cdot \varrho^r = \sum_{p} E_{\varrho}^{(p)} \cdot \delta^p = \sum_{r} E_{\delta}^{(r)} \cdot \varrho^r. \tag{2}$$

We may now express $\Delta \boldsymbol{R}_e$ as a functional of ΔH with the help of the double perturbation energies $E^{(p,r)}$ (see Sect. 3).

The variation of the electron-nuclear potential V_{ne} with variation of the nuclear positions $\boldsymbol{R}$ has a disadvantageous power expansion in δ. Assume, for instance, a nucleus with change $+Ze$ at the origin, which is shifted by $\boldsymbol{dZ}$ in the z-direction. Then, for $dZ < r$

$$V_{ne} = -Ze^2/|\boldsymbol{r} - \boldsymbol{dZ}| = -\sum_{p=0}^{\infty} (P_p(\cos\theta) \cdot Ze^2/r^{p+1}) \cdot dZ^p. \tag{3}$$

First, the potential operator V_{ne} contains an infinite number of perturbation terms of all orders dZ^p and $p = 1, 2, 3, \ldots$. *Second*, the perturbation of the potential V_{ne} (due to $\pi \cdot \Delta R_e$) appears both in the nonrelativistic Hamiltonian H_0 an in its relativistic correction, $\varrho \cdot \Delta H$, see Eq. (1). Accordingly, the Hamiltonian H contains an infinite number of mixed perturbations $\sim \varrho \cdot dZ^p$, first order in relativity and pth order in the change of structure, with $p = 0$ and also with $p = 1, 2, 3, \ldots$. *Third*, the singular perturbation terms $\sim P_p(\cos\theta)/r^{p+1}$ in the Hamiltonian result in singular perturbation functions, which are not easily representable in standard basis sets. A differential shift of the nuclei requires a corresponding shift of the basis functions. For instance, in first order because of

$$\frac{\partial}{\partial Z} e^{-\alpha|\boldsymbol{r} - \boldsymbol{R}|} = \frac{z - Z}{r} e^{-\alpha|\boldsymbol{r} - \boldsymbol{R}|},$$

a so-called $1p$-function is needed in the case of a $1s$ basis function (compare the similar case of the calculation of nonadiabatic coupling elements, gradients etc.). More singular basis functions are required for the higher order perturbation functions. Even worse, the perturbation expressions contain several contributions of opposite sign which, when not analytically kept together, will lead to divergent integrals [1, 2].

Therefore, we look for a transformation so that:

(1) the perturbation consists of only a single linear term in δ, and
(2) the perturbation potential and perturbation functions are less singular.

This will be achieved in Sect. 2 by rescaling techniques.

For heavy atoms, relativistic effects become important in the valence shell. Having appropriate perturbation expressions at hand for the derivatives of the molecular potential hypersurface, we can investigate its change due to relativity [1, 3]. Expressions which are easy to apply in numerical calculations are presented in Sect. 3.

These expressions are then used to determine the relativistic corrections of the bond length R_e, of the force constant k, and of the anharmonicity constant a, of the H_2^+ molecular ion. Accurate results are presented in Sect. 4.

2 Scaling of the molecular one-electron equation

Within the framework of the Born–Oppenheimer clamped nuclei approximation, we write the Dirac equation in the form [1, 2]:

$$\left[\{V_{ne} - E_{el}(\varrho)\} \cdot \begin{pmatrix} 1 & 0 \\ 0 & \varrho/c^2 \end{pmatrix} + \begin{pmatrix} 0 & \boldsymbol{\sigma p} \\ \boldsymbol{\sigma p} & -2m \end{pmatrix}\right] \cdot \begin{pmatrix} \psi_+ \\ \tilde{\psi}_- \end{pmatrix} = 0 \tag{4}$$

with nuclear-electron potential energy:

$$V_{ne} = -\sum_i e^2 Z_i / |\boldsymbol{R}_i - \boldsymbol{r}| \tag{5}$$

and $\varrho = 1$ for the relativistic case, $\varrho = 0$ for the nonrelativistic case, i.e.:

$$\left\{V_{ne} - E_{el}(\varrho = 0) + \boldsymbol{\sigma p}\frac{1}{2 \cdot m}\boldsymbol{\sigma p}\right\}\psi_+ = 0. \tag{4nr}$$

The total energy at internuclear distance $R = |\boldsymbol{R}_1 - \boldsymbol{R}_2|$ is:

$$E_T(\varrho, R) = E_{el}(\varrho, R) + e^2 Z_1 Z_2 / R. \tag{6}$$

The second term in Eq. (4) is the (relativistic or nonrelativistic) kinetic energy operator T in four-component representation, and $\tilde{\psi}_- = c \cdot \psi_-$ (i.e. change of metric as proposed by Kutzelnigg [2c]).

At the relativistic internuclear distance:

$$R'_e = R^0_e + \Delta R_e = R^0_e \cdot \gamma, \quad \text{i.e. } \gamma = 1 + \Delta R_e / R^0_e = 1 + \delta, \tag{7}$$

where R_e is the nonrelativistic bond length, $\delta = \Delta R_e / R$ is the fractional relativistic change of bond length which may be positive or negative, Eq. (4) reads:

$$\left[\{V_{ne}(R'_e, \boldsymbol{r}) - E_{el}(\varrho, R'_e)\} \cdot \begin{pmatrix} 1 & 0 \\ 0 & \varrho/c^2 \end{pmatrix} + \begin{pmatrix} 0 & \boldsymbol{\sigma p} \\ \boldsymbol{\sigma p} & -2m \end{pmatrix}\right] \cdot \begin{pmatrix} \psi'_+ \\ \tilde{\psi}'_- \end{pmatrix} = 0. \tag{8}$$

The nonrelativistic analog for $\varrho = 0$ is simply:

$$\{V_{ne}(R^0_e, r) - E_{el}(\varrho = 0, R^0_e) + p^2/2m\}\psi_+ = 0. \tag{8nr}$$

Equations (3, 4, 8) had been used in Ref. [1] to determine ΔR_e. In order to solve these equations accurately for the higher perturbation energies in a finite basis set, the basis functions must be selected very carefully because of the reasons mentioned in the introduction. Therefore we now look for a coordinate transformation so that the nuclear displacement parameter does no longer appear in all orders, as dZ in Eq. (3), but simply scales either (a) the potential or (b) the kinetic energy operator, respectively, in Eq. (4) in a *linear* manner. Generalizing the nonrelativistic approach of Cohen and McEachran [8], we substitute:

$$r = r' \cdot \gamma, \qquad \varrho = \varrho' \cdot \gamma^2, \qquad \tilde{\psi}'_- = \psi'_- / \gamma, \tag{9}$$

into Eq. (8) and obtain:

$$\left[\{V_{ne}(R^0_e, \boldsymbol{r}')/\gamma - E_{el}(\varrho'\gamma^2, R^0_e\gamma)\} \cdot \begin{pmatrix} 1 & 0 \\ 0 & \varrho'\gamma/c^2 \end{pmatrix} + \begin{pmatrix} 0 & \boldsymbol{\sigma p}'/\gamma^2 \\ \boldsymbol{\sigma p}'/\gamma & -2m/\gamma \end{pmatrix}\right] \cdot \begin{pmatrix} \psi'_+ \\ \psi'_- \end{pmatrix} = 0. \tag{10}$$

Note that scaling distances ($r \rightarrow r'$) will automatically scale also the velocities ($\varrho/c^2 \rightarrow \varrho'/c^2$). This change of scale is defined so that the *nuclear positions do not change* their numerical values upon relativistic change of bond length. Then the basis functions also need not be shifted, and no singular functions such as $(d/dR_e)(1s)$ etc. are required.

Multiplying the upper and lower lines, respectively, (a) by γ^2 and γ^1, or (b) by γ^1 and γ^0, we obtain:

(a) either (upon introducing $\delta = \gamma - 1$, where δ is the fractional change of internuclear distance, $\Delta R_e / R_e^0$, see above):

$$\left[\{(1+\delta) \cdot V_{ne}(R_e^0, \mathbf{r}') - \epsilon_{el}(\delta, \varrho', R_e^0)\} \cdot \begin{pmatrix} 1 & 0 \\ 0 & \varrho'/c^2 \end{pmatrix} + \begin{pmatrix} 0 & \boldsymbol{\sigma p}' \\ \boldsymbol{\sigma p}' & -2m \end{pmatrix}\right] \cdot \begin{pmatrix} \psi'_+ \\ \psi'_- \end{pmatrix} = 0 \tag{11a}$$

with

$$E_T(\varrho, R_e^0 + \Delta R_e) = e^2 \cdot Z_1 \cdot Z_2 / \gamma R_e^0 + \epsilon_{el}(\delta, \varrho/\gamma^2, R_e^0)/\gamma^2, \tag{12a}$$

(b) or (upon introducing $\tau = \gamma^{-1} - 1$, where $\tau = -\Delta R_e / (R_e^0 + \Delta R_e)$):

$$\left[\{V_{ne}(R_e^0, \mathbf{r}') - \eta_{el}(\tau, \varrho', R_e^0)\} \cdot \begin{pmatrix} 1 & 0 \\ 0 & \varrho'/c^2 \end{pmatrix} + (1+\tau) \cdot \begin{pmatrix} 0 & \boldsymbol{\sigma p}' \\ \boldsymbol{\sigma p}' & -2m \end{pmatrix}\right] \cdot \begin{pmatrix} \psi'_+ \\ \psi'_- \end{pmatrix} = 0 \tag{11b}$$

with

$$E_T(\varrho, R_e^0 + \Delta R_e) = e^2 \cdot Z_1 \cdot Z_2 / \gamma R_e^0 + \eta_{el}(\tau, \varrho/\gamma^2, R_e^0)/\gamma. \tag{12b}$$

With the help of the coordinate transformation of Eq. (9), the complicated expression of the perturbed potential is simplified to contain only a first and/or a zeroth order term, respectively. Since the relativistic perturbation of order ϱ/c^2 in Eq. (4) contains just $(V_{ne} - E_{el})$, this coordinate transformation is equally useful in the nonrelativistic and relativistic cases. The perturbation becomes simply $\delta \cdot V_{ne}$ in Eq. (11a) corresponding to a change of distances, or $\tau \cdot T$ in Eq. (11b) corresponding to a change of velocities. The perturbed equations contain *only a single linear perturbation of the unshifted positions* R_e^0 of the nuclei, but with modified velocity of light $c \cdot \gamma$ [i.e. $\varrho'/c^2 = \varrho/(c \cdot \gamma)^2$] and

(a) either with modified nuclear charge $Z_i \cdot \gamma = Z_i \cdot (1 + \delta)$ (Eq. 11a),
(b) or with modified electronic mass $m/\gamma = m \cdot (1 + \tau)$ (Eq. 11b).

Therefore the perturbed wavefunctions will easily be representable in standard basis sets.

Expanding now E_T from Eqs. (12a,b) in ϱ, and in δ or τ, respectively, and equating with the expansion of E_T from Eqs. (2, 6), we obtain:

$$E^{(p,r)} = (-1)^p \cdot \left[\delta_{0,r} \cdot \frac{Z_1 Z_2}{R_e} \cdot e^2 + \sum_{i=0}^{p} (-1)^{p-i} \cdot \binom{2r+i+1}{i} \cdot \epsilon_{el}^{p-i,r}\right] \tag{13a}$$

$$= (-1)^p \cdot \left[\delta_{0,r} \cdot \frac{Z_1 Z_2}{R_e} \cdot e^2 + \sum_{i=0}^{p} \binom{2r+p}{i} \cdot \eta_{el}^{p-i,r}\right]. \tag{13b}$$

The $E^{(p,r)}$-perturbation terms are thus expressed as sums of the terms $\epsilon_{el}^{p,r}$ or $\eta_{el}^{p,r}$, which are easily obtained from the perturbation equations for the $\epsilon^{p,r}$:

$$\sum_{j=0}^{p} \sum_{i=0}^{r} (H^{p,r} - \epsilon^{p,r} \cdot \beta^+ - \epsilon^{p,r-1} \cdot \beta^-) \cdot \psi^{p-j,r-i} = 0 \tag{14a}$$

or from identical equations "(14b)" for the $\eta^{p,r}$, with:

$$\epsilon^{p,-1} = \eta^{p,-1} \equiv 0, \tag{15}$$

and

$$\beta^{+}=\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix},\qquad \beta^{-}=\begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix},$$

$$H^{00}=\beta^{+}\cdot V_{ne}+(\boldsymbol{\alpha}\cdot\boldsymbol{p}-2\beta^{-}\cdot m)=\beta^{+}\cdot V_{ne}+T, \tag{16}$$

$$H^{01}=\beta^{-}\cdot V_{ne}.$$

For cases (a) and (b), respectively,

$$H^{10}=\beta^{+}\cdot V_{ne},\qquad H^{11}=\beta^{-}\cdot V_{ne}, \tag{17a}$$

and

$$H^{10}=T. \tag{17b}$$

All other $H^{p,r}$ vanish. Explicit formulae for the $\epsilon^{p,r}$ and $\eta^{p,r}$ may then be obtained as in Ref. [1] for the $E^{(p,r)}$.

3 Relativistic changes of bond length, force constant and anharmonicity

Knowing the expansion of Eq. (2) from Eqs. (13a,b), it is easy to determine the relativistic changes of bond length ΔR_e, of force constant Δk, of lowest order anharmonicity Δa, etc. The nonrelativitstic and relativistic molecular structures are *implicitly* given, resp., by:

$$R_e^0:\quad (dE_T/d\delta)_{\delta=0,\varrho=0}=0, \tag{18}$$

$$\Delta R_e:\quad (dE_T/d\delta)_{\delta=\Delta R_e/R_e^0,\varrho=1}=0. \tag{19}$$

This means: $\partial E_T(\varrho=0, R_e^0)/\partial R=0$ and $\partial E_T(\varrho=1,(1+\delta)\cdot R_e^0)/\partial R=0$, which defines a function between the relativistic parameter ϱ and the bond length parameter δ. From Eqs. (2, 9) then following:

$$\Delta R_e=\alpha_0+\sum_{p=2}^{\infty}\alpha_p\cdot\Delta R_e^p, \tag{20}$$

where we have introduced the abbreviation:

$$\alpha_p=-(p+1)\cdot E_{\varrho=1}^{(p+1}/(2E_{\varrho=1}^{(2)}\cdot R_e^{p-1}). \tag{21}$$

Equation (20) can be solved by recursion

$$\begin{aligned}\Delta R_e=\alpha_0(1+\alpha_0(\alpha_2+&\\ &\alpha_0(\alpha_3+2\alpha_2^2+\\ &\alpha_0(\alpha_4+5\alpha_3\alpha_2+5\alpha_2^3+\\ &\alpha_0(\alpha_5+6\alpha_4\alpha_2+3\alpha_3^2+21\alpha_3\alpha_2^2+14\alpha_2^4+\\ &\alpha_0(\alpha_6\ldots.\end{aligned} \tag{22}$$

The corresponding equations for force constant and anharmonicity read (with $\beta_i=E_{\varrho=0}^{(i+1)}/E_{\varrho=1}^{(i+1)}$):

$$\begin{aligned}\Delta k=2E_{\varrho=1}^{(2)}/R_e^2\cdot(1-\beta_1-\alpha_0(2\alpha_2+&\\ &\alpha_0(3\alpha_3+2\alpha_2^2+\\ &\alpha_0(4\alpha_4+8\alpha_3\alpha_2+4\alpha_2^3+\\ &\alpha_0(5\alpha_5+14\alpha_4\alpha_2+6\alpha_3^2+25\alpha_3\alpha_2^2+10\alpha_2^4+\\ &\alpha_0(6\alpha_6+\cdots\end{aligned} \tag{23}$$

$$\begin{aligned}\Delta a = -4E^{(2)}_{\varrho=1}/R_e^2 \cdot \{\alpha_2(1-\beta_2) + \alpha_0(3\alpha_3 + {} & \\ & \alpha_0(6\alpha_4 + 3\alpha_3\alpha_2 \\ & \alpha_0(10\alpha_5 + 12\alpha_4\alpha_2 + 3\alpha_3^2 + 6\alpha_3\alpha_2^2 + \\ & \alpha_0(15\alpha_6 + \cdots .\end{aligned} \tag{24}$$

4 Application to the $1\sigma_g$ state of H_2^+

The present formalism has been applied to the ground state of H_2^+ in a finite Gaussian basis set. At first we comment on the possible accuracy of the calculated perturbation energies, E^{11} being a simple example. Since for any real expectation value

$$\langle\psi|A|\psi\rangle = \langle\psi|A|\psi\rangle^* = \langle\psi|A^+|\psi\rangle, \tag{25}$$

we may write

$$\langle\psi^{00}|\tilde{H}^{10}\cdot\frac{1}{\tilde{H}^{00}}\tilde{H}^{01}|\psi^{00}\rangle = \langle\psi^{00}|\tilde{H}^{01}\cdot\frac{1}{\tilde{H}^{00}}\tilde{H}^{10}|\psi^{00}\rangle \tag{26}$$

where $\tilde{H}\psi$ is an abbreviation for $(H-E)\psi$. Inserting $\tilde{H}^{01}\psi^{00} = -\tilde{H}^{00}\psi^{01}$ and $\tilde{H}^{10}\psi^{00} = -\tilde{H}^{00}\psi^{10}$, Eq. (26) becomes identical with the double perturbation theorem:

$$\langle\psi^{00}|\tilde{H}^{10}|\psi^{01}\rangle = \langle\psi^{00}|\tilde{H}^{01}|\psi^{10}\rangle. \tag{27}$$

If ψ^{00}, ψ^{01} and ψ^{10} are all approximated in the same basis, that is if all $\tilde{H}$'s are represented in the same basis, then Eq. (26) and therefore also Eq. (27) holds exactly. This is so even if the basis is only sufficient to represent ψ^{00} accurately while being too small to approximate ψ^{01} or ψ^{10} reasonably well, so that the matrix elements in Eqs. (26, 27) may both be quite inaccurate, but still equal. To turn it around, in order to calculate accurate perturbation energies, all *operators* must be represented in an extended basis which is sufficient to approximate all functions which they generate, even if they do not appear explicitly, as e.g. in Eq. (26).

For the nonrelativistic $1\sigma_g$-state of H_2^+, σ_g AOs on the molecular axis are sufficient to represent the *upper* component ψ^{00}_+, which is just the usual Schrödinger wavefunction. We have used 27 Gaussian *s*-lobe functions of α-spin (symmetrized to yield σ_g MOs) with partially optimized positions and exponents between $5.0E8$ and 0.08 (see [2b] and appendix), and 12 cartesian Gauss-$p\sigma$ AOs with the same exponents between $3.5E7$ and $1.5E1$. For extended calculations, one $s\sigma$, 9 $p\sigma$, 14 $d\sigma$ and 14 $f\sigma$ functions of the general form:

$$\chi_i = z_i^n \cdot \exp(-\zeta_i \cdot r_i^2) \cdot \alpha \tag{28}$$

were added, which changed the results only slightly (see "large basis" in Table 1). The same bases were used for ψ^{10}_+.

Relativistic spin-orbit coupling mixes $\sigma_g^{1/2}$ with $\pi_g^{1/2}$ (compare Sundholm et al. [4]). Accordingly π AOs with β-spin are needed in addition for ψ^{01}_+:

$$\chi_j = (x_j + iy_j) \cdot z_j^n \cdot \exp(-\zeta_j \cdot r_j^2) \cdot \beta. \tag{29}$$

For the $p\pi$ and $d\pi$ AOs of the "small" basis, the same exponents were chosen as for the $s\sigma$ and $p\sigma$ AOs, and also for the $f\pi$ and $g\pi$ ones of the "large" basis. The

Table 1. Perturbation energies of H_2^+ in a.u.

Basis	Method of Ref. [1], Eqs. (3, 4)		Present method, Eqs. (11)		Large basis	Most reliable literature data[c]
	$27s$[a]	$64s$[a]	$27s + 12p\sigma$	$27s + 12p\sigma + 27p\pi + 12d\pi$		
R_e^{nr}	1.997 192	1.997 192	1.997 1933	1.997 1933	1.997 1933	1.997 193 [6]
E^{00}	−.602 6343	−.602 6346	−.602 634 62	−.602 634 62	−.602 634 629	−.602 643 62 [6] −.602 634 6 [9^d] −.602 634 629 [10]
E^{10}	0	0	0	0	0	
E^{20}	0.051 450	0.051 568	0.051 4854	0.051 4854	0.051 485 23	0.051 5 [6] 0.051 3 [9^d]
E^{30}	−.043 632	−.043 89	−.043 5305	−.043 5305	−.043 5307	
E^{40}			0.026 6355	0.026 6355	0.026 6354	
E^{50}			−.014 7515	−.014 7515	−.014 7515	
$E^{01} \cdot c^2$	−.138 531	−.138 534	−.138 5338	−.138 5338	−.138 533 96	−.138 533 97 [10] −.138 534 [9^d]
$E^{11} \cdot c^2$	0.071 75	0.071 751	0.071 7639	0.071 7639	0.071 7686	0.071 772 [9^d]
$E^{21} \cdot c^2$	−.044 9[b]	−.055 08[b]	−.057 4612	−.057 4612	−.057 4616	−.06 [3, 6] −.057 32 [9^d]
$E^{31} \cdot c^2$			0.032 746	0.032 746	0.032 747	0.031 5 [9^d]
$E^{41} \cdot c^2$			−.017 313	−.017 313	−.017 314	
$E^{02} \cdot c^4$	−.040 394	−.040 405	−.040 395	−.041 7152	−.041 7255	−.041 723 52 [10]
$E^{12} \cdot c^4$	−.002 4	−.002 412	−.002 358	−.000 9517	−.000 9275	
$E^{22} \cdot c^4$				−.006 095	−.006 0803	
$E^{32} \cdot c^4$				0.004 732	0.004 712	
$E^{03} \cdot c^6$	−.027 83	−.027 841	−.027 852	−.028 3105	−.028 3117	−.028 311 6 [10]
$E^{13} \cdot c^6$				−.002 286	−.002 278	
$E^{23} \cdot c^6$				−.001 502	−.001 479	
DE^{nr}	−.101 9313	−.101 9326	−.101 9320	−.101 9320	−.101 9326	
k^{nr}	0.102 9	0.103 1	0.102 971	0.102 971	0.102 970	0.103 0 [6]
a^{nr}	−.261 8	−.261 6	−.261 183	−.261 183	−.261 184	
$\Delta R/R \cdot c^2$	−.349	−.348 34	−.348 961	−.348 961	−.348 985	
$\Delta DE/DE \cdot c^2$	0.132 8	0.132 78	0.132 7743	0.132 7763	0.132 7765	
$\Delta k/k \cdot c^2$	0.901	0.693	0.651 72	0.651 839	0.651 839	
$\Delta a/a \cdot c^2$				0.953 64	0.953 64	

[a] Floating Gaussians, carefully optimized for ψ^{00}, ψ^{10} and ψ^{01}

[b] The value for $E^{21} \cdot c^2$ was given erroneously as $+0.7$ in Ref. [1a], the rather correct value of $-.0449$ given above is from Ref. [1b] (see second line of Eq. (4.15) in Ref. [1b]; note the reversed order of indices used there)

[c] Relativistic perturbation energies for $R = 2$, corrected for the nonrelativistic equilibrium distance 1.997 193, with the help of the present mixed perturbation terms ($E^{i,j}(R_e) = E^{i,j}(R = 2) - 0.002807 \cdot E^{i+1,j}$)

[d] Determined by fitting polynomials of R and c^2 to the numerical results of [9]

basis functions for the *lower* components of the ψ's were constructed implicitly by operating with $\boldsymbol{\sigma} \cdot \boldsymbol{p}$ on the χ's (so called kinetically balanced basis). Using the notation:

$$E^{p,r} = E^{(p,r)} \cdot R_e^{-p} \tag{30}$$

the perturbation energies for $p + r \leqslant 3$ were then calculated algebraically within the framework of double perturbation theory based on Eqs. (11, 13). Higher orders in the first superscript were then estimated by the finite perturbation approach: Perturbation energies $E^{p,r}$ for $p + r = 3$ were calculated at $n = 4$

additional points in the neighborhood of the nonrelativistic equilibrium distance R_e ($\delta R = 0.02a_0$) and then fittted by a polynomial

$$E^{p,r}(R_e + d) = \sum_{i=0}^{n} G^{(i)} \cdot d^i. \tag{31}$$

The higher order perturbation energies are then obtained as

$$E^{p+i,r}(R_e) = G^{(i)} \bigg/ \binom{p+i}{p}. \tag{32}$$

The present results, up to fifth order, are presented in Table 1 and compared with previous results from Eqs. (3, 4) in Ref. [1]. Concerning the pure relativistic perturbation energies, our results are in excellent agreement with the most recent results of other authors [4, 5, 6, 9, 10].

5 Discussion

We treat molecular geometry changes and relativistic corrections as two simultaneous perturbations. In the unscaled original approach (Eqs. (3, 4)), extended basis sets containing $\partial^m f_n(R, r)/\partial R^m$ in addition to f_n are required in order to obtain high accuracy for the higher order perturbation energies, especially those of mixed type. With the present method (Eqs. 11a/b) we have easily obtained quite accurate results with nonextended bases (see Table 1). The relativistic perturbation is expressed by simply scaling either the potential or the kinetic energy. Both approaches yield exactly the same results also for finite basis sets. Because of its simplicity, the kinetic energy approach is more recommendable. The approach can be extended to many electron systems, but only to the overall breathing mode of polyatomic molecules.

We note that it is very important for the higher order relativistic perturbation energies to include π-orbitals in the basis for the relativistic correction of the σ_g wavefunction, ψ_+^{01}, even though $1\sigma_g$ is mainly of $1s$ character [11]. Concerning E^{21}, some previous literature values were not very accurate (see Table 2), while the value of $E^{21} \cdot c^2 = -0.06$ obtained by standard Pauli perturbation theory [3] is reasonable.

Having for the first time accurate high order *mixed* energy corrections at hand, we may employ the equations of Sect. 3 to calculate the relativistic changes of bond length, ΔR, of force constant, Δk, and of anharmonicity, Δa. The relativistic change Δ of an *equilibrium property* $p(R_e)$ consists of two contributions. At lowest order:

$$\Delta p_e = \Delta^{\text{dir}} p_e + \Delta^{\text{ind}} p_e \approx (\partial p/\partial \varrho)_{R_e^0} + (\partial p/\partial R)_{R_e^0} \cdot \Delta R_e. \tag{33}$$

The first "direct" contribution is the direct relativistic change at the nonrelativistic molecular equilibrium geometry. The second "indirect" contribution is the change of the nonrelativistic property due to the relativistic change of the equilibrium geometry. The accurate determination of relativistic changes of bond length and other R-dependent properties was achieved by a scale transformation of the relativistic Hamiltonian so that it has the same (scaled) equilibrium bond length as the nonrelativistic one.

Concerning the bond energy, the first order direct relativistic contribution $\Delta DE(R_e^0) = E^{01} + 1/8c^2 = -0.0135/c^2$ dominates. Since the energy is stationary at R_e, the indirect term $k/2 \cdot \Delta R^2 = -0.025/c^4$ is only of second order in $(1/c^2)$.

Table 2. Relativistic change of force conswtant of H_2^+ at R_e^0 and R_e^{rel}

$\Delta^{\mathrm{rel}}k/k \cdot c^2$	obtained from reference:
$-1.$	[3] (analytical pert., without indirect correction: Luke et al. 1969; Bishop 1977)
$+0.6$	(ditto, corrected for ΔR_e with our E^{ij} from Table 1)
$+8$	[4] (finite difference, finite perturbation: Sundholm 1987/1988)
$+0.6$	[6] (finite difference, finite pert., improved accuracy: Sundholm 1990)
$+13.6$	[1a] (new rel. pert. approach, original Eqs. (3, 4): these authors 1990, small basis)
$+0.9$	[lb] (ditto, improved basis set: these authors 1991)
$+0.652$	present work (finite perturbation approach of Eqs. (3, 4))
$+0.651839$	present work (algebraic solution of the scaled Eqs. (11))

More important are the nonadiabatic corrections ($-0.13\ \mathrm{cm}^{-1}$ for the ground state [11]), which are comparable to the relativistic corrections ($\Delta DE = -0.16\ \mathrm{cm}^{-1}$).

In the case of the force constant, the direct term is $\approx 2E^{21} = -0.115/c^2$, i.e. *relativity tends to reduce the force constant*, although it increases the value of the bond energy. On the other hand, the *relativistic bond contraction tends to increase the force constnat*, due to the nonrelativistic anharmonicity, by $\approx -3E^{30}/E^{20}E^{11} = +0.18/c^2$. So the latter indirect term is dominant and determines the sign of $\Delta k \approx +0.065/c^2$. Many different values of Δk have been published previously by different authors, including the present ones, see Table 2. Our present results corroborate the improved value of Sundholm [6].

Concerning the anharmonicity, we get $\Delta a \approx 6E^{31} - 12E^{40}/E^{20}E^{11} = +0.20/c^2 - 0.45/c^2 = -0.25/c^2$. Again, the change of the nonrelativistic anharmonicity due to relativistic change of geometry is the dominant contribution and determines the sign of Δa.

The relativistic results on H_2^+ confirm several empirical *nonrelativistic* rules [7], according to which contraction of bond length ($-\Delta R/R > 0$), increase of bond energy ($\Delta DE/DE > 0$) and increase of force constant ($\Delta k/k > 0$) should go in parallel. We find for H_2^+: $-\Delta R/R = +0.35/c^2$, $\Delta DE/DE = +0.13/c^2$ and $\Delta k/k = +0.65/c^2$. This is in agreement with Badger's rule [7], namely $-\Delta R = \mathrm{const} \cdot \Delta k$, and with Gordy's ruyle [7], $\Delta DE/DE = -\mathrm{const} \cdot \Delta R$. The significant increase of force constant corresponds to the significant increase of anharmonicity, $\Delta a/a = +0.95/c^2$. Without the dominance of the indirect term, i.e. the change of the *nonrelativistic* property with ΔR, the empirical rules would not hold for the relativistic effects.

In general, in a homologous series of molecules from one column (i) of the periodic system, fractional relativistic corrections of properties p, ($\Delta p/p$), vary as:

$$\Delta p/p \approx f_p^{(i)} \cdot (Z/c)^2, \tag{34}$$

where Z is the unscreened nuclear charge. Since for H_2^+, $f_k = 0.65$ and $f_a = 0.95$, it is to be expected that diatomics of heavy monovalent atoms will show large relativistic increase of force constant and anharmonicity. While the relativistic effects in alkali compounds are rather small, the force constants of Ag- and Au-diatomics are drastically increased by relativity, in general by more than 40% and 100%, respectively, which corresponds to a factor of $f_k > 3$.

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Appendix

Slater $1s\sigma$ AO Basis for H_2^+ at $R_i = \pm 0.998\,596\,666$

Exponent		Position ($\pm R$)	Exponent	Position ($\pm R$)
5.1	*E*8	0.998 596 666	6.927 028 155	0.910 502 569
3.5	*E*7	0.998 596 666	3.385 482 480	0.977 711 646
3.5	*E*6	0.998 596 666	2.402 017 358	0.539 998 793
4.325 462 323	*E*5	0.998 569 622	1.638 810 974	0.972 176 073
6.435 495 511	*E*4	0.998 595 065	1.097 934 991	0.500 614 471
1.466 468 048	*E*4	0.998 592 652	0.806 993 599	0.954 213 294
4.148 358 545	*E*3	0.998 575 946	0.547 494 371	0.292 511 401
1.347 714 185	*E*3	0.998 544 440	0.465 648 655	0.139 775 858
4.847 182 609	*E*2	0.998 433 731	0.424 455 286	0.861 735 833
1.886 351 270	*E*2	0.998 210 678	0.260 149 113	0.208 653 824
7.799 136 410	*E*1	0.997 583 355	0.246 597 597	0.930 799 165
3.386 610 720	*E*1	0.996 418 608	0.144 508 470	0.671 011 270
1.529 945 884	*E*1	0.993 207 282	0.080 512 889	0.709 988 965
7.187 774 935		0.999 419 237		