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Relativistic perturbation theory of chemical properties

A. Rutkowski* and W. H. E. Schwarz
Theoretische Chemie, Universität Siegen, POB 10 12 40, D-5900 Siegen,
Federal Republic of Germany

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Summary. Double perturbation theory is developed for the case where relativity is one perturbation and the other perturbation describes a chemically interesting observable such as molecular structure, force constant or polarizability. Relativity is treated according to Rutkowski's nonsingular perturbation approach. Expressions for four-component and two-component wavefunctions and for the Hartree-Fock approximation are given. The method is applied analytically to the relativistic corrections of the electric polarizability of the H atom, and algebraically to the potential curve of the H_2^+ molecule. Second and third order double perturbation interchange relations are numerically verified. In the present formalism, terms up to third order are needed to qualitatively understand the relativistic corrections of chemical observables.

Key words: Double perturbation theory — Relativistic corrections — H_2^+ — Polarizability of H

1. Introduction

Chemistry is governed by the valence electrons. Their behavior is qualitatively determined by the screened nuclear charges Z_{eff} and the atomic quantum numbers n, l and κ. For instance, the valence orbital energy ϵ_{val} may be represented by

$$\epsilon_{\text{val}} = -0.5(Z_{\text{eff}}/n)^2, \tag{1.1}$$

where (Z_{eff}/n) is of order 1 for the valence shells of all atoms.

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* *Permanent address*: Division of Physics, Higher Pedagogical School, Zolnierska 14, PL-10561 Olsztyn, Poland

For atoms from the lower rows of the periodic table, relativistic corrections significantly modify the nonrelativistic expectation values a^{nrel}. We define the total and relative relativistic corrections, $\Delta^{\mathrm{rel}}a$ and $\delta^{\mathrm{rel}}a$, respectively by

$$\delta^{\mathrm{rel}}a = \Delta^{\mathrm{rel}}a/a^{\mathrm{nrel}} = (a^{\mathrm{rel}} - a^{\mathrm{nrel}})/a^{\mathrm{rel}}. \tag{1.2}$$

δ^{rel} depends, to a good approximation only on the *unshielded* nuclear charge Z rather than on Z_{eff} and n, so that we may write

$$\delta^{\mathrm{rel}}a_{\mathrm{core\ or\ val}} \approx \mathrm{const}_\kappa \cdot (Z/c)^2, \tag{1.3}$$

where c is the velocity of light (in atomic units $c = 1/\alpha = 137.037$) and const_κ is a parameter mainly depending on the type (quantum number κ) of the bond-active valence shell, or in chemical terms, on the group number of the atom in the periodic table. The physical reason for the unexpectedly large relativistic corrections found empirically even for the valence shells has recently been explained by Schwarz et al. [1, 2].

The basic chemical properties, a, of molecules are geometrical structure, energetic stability, and electromagnetic moments and responses. Let ϱ be the relativistic parameter, i.e. $\varrho = 0$ for a nonrelativistic formalism and $\varrho = 1$ for a relativistic one. Expanding a in a Taylor series of ϱ, we obtain to lowest orders

$$\Delta^{\mathrm{rel}}a = (da/d\varrho)_0 + \tfrac{1}{2}(d^2a/d\varrho^2)_0 + \cdots \approx \tfrac{1}{2}[(da/d\varrho)_0 + (da/d\varrho)_1], \tag{1.4}$$

$$\delta^{\mathrm{rel}}a = (d \ln a)/d\varrho)_0 + \tfrac{1}{2}[(d^2 \ln a/d\varrho^2)_0 + (d \ln a/d\varrho)_0^2] + \cdots \tag{1.5}$$

where the indices 0 and 1 indicate the value of ϱ where the derivatives are taken. The chemical properties may be classified as *direct* expectation values (dipole moments, transition moments), as *difference* properties (bond energy, activation energy, ionization potential), or as *differential* properties (geometric structure, force constant, polarizability). The latter ones are defined via derivatives. For instance, the geometric parameters γ (bond lengths R, bond angles β) are defined by $dE/d\gamma = 0$. The force constant is $k = d^2E/d\gamma^2$, the electric dipole polarizability is $\alpha_d = d^2E/dF^2$.

The physical origin of relativistic corrections to *direct* and *difference* properties has been discussed in the literature (see, e.g., [1–6]) and seems to be understood to some extent. To low order, the relativistic corrections to the polarizability α, force constant k and anharmonicity x are given by

$$\Delta^{\mathrm{rel}}\alpha = (\partial^3E/\partial F^2\,\partial\varrho) + \tfrac{1}{2}(\partial^4E/\partial F^2\,\partial\varrho^2) + \cdots, \tag{1.6}$$

$$\Delta^{\mathrm{rel}}k = (\partial^3E/\partial\gamma^2\,\partial\varrho) + \tfrac{1}{2}(\partial^4E/\partial\gamma^2\,\partial\varrho^2) + \cdots, \tag{1.7}$$

$$\Delta^{\mathrm{rel}}x = (\partial^4E/\partial\gamma^3\,\partial\varrho) + \cdots. \tag{1.8}$$

For geometric parameters γ we obtain, expanding E up to third order, and solving $\partial E/\partial\gamma = 0$ to the appropriate order,

$$\Delta^{\mathrm{rel}}\gamma \approx -A/k \cdot (1 + xA/2k^2), \tag{1.9}$$

where

$$A = (\partial^2E/\partial\gamma\,\partial\varrho)_0 + \tfrac{1}{2}(\partial^3E/\partial\gamma\,\partial\varrho^2)_0 + \cdots, \tag{1.10}$$

is the slope of the relativistic potential hypersurface at the nonrelativistic equilibrium position.

Relativistic corrections to *differential* properties have been investigated, both numerically (for a literature collection see Pyykkö [3]) and formally [1, 4, 7, 8]. However, the formal analysis has so far only been carried through to second order, although it is evident from the numerical work that third order terms must not be neglected even at a qualitative level. For instance, the relativistic correction to the force constant (Eq. 1.7) turns out to be qualitatively important. Nevertheless, $\Delta^{\mathrm{rel}}k$ has not yet been investigated theoretically. One should at least achieve a physical understanding of the signs of $\Delta^{\mathrm{rel}}k$.

The partial derivatives introduced above are related to the energy coefficients $E^{i,j}$ of double perturbation theory. The first perturbation is the perturbation of the potential due to an external field, F, or to a change of the molecular structure, γ. The second one is the relativity, ϱ. Accordingly, we obtain

$$\Delta^{\mathrm{rel}}k = 2(E^{2,1} + E^{2,2} + \cdots), \qquad \delta^{\mathrm{rel}}k = (E^{2,1} + E^{2,2} + \cdots)/E^{2,0} \tag{1.11}$$

and similar expressions for $\Delta^{\mathrm{rel}}\alpha$, $\Delta^{\mathrm{rel}}x$, etc., and from Eq. (1.9)

$$\Delta^{\mathrm{rel}}\gamma = -E^{1,1}/2E^{2,0} \cdot (1 - E^{2,1}/E^{2,0} + E^{1,2}/E^{1.1} + 0.75 \cdot E^{3,0}E^{1,1}/E^{2,0}E^{2,0} + \cdots). \tag{1.12}$$

In this work we shall determine the double perturbation theory expressions up to third order, using Rutkowski's [9] convergent relativistic perturbation approach. The general formulae for four-component wavefunctions are derived in Sect. 2. In an appendix, explicit formulae are given which use only the upper two-component wavefunctions as they are more convenient in numerical calculations than the four-component ones. Furthermore, the independent particle approximation is introduced, whereby the wavefunctions are represented by single determinants of 2-component molecular spinors.

In Sect. 3, the formalism is applied to *analytically* calculate the perturbed energy and wavefunction for a relativistic hydrogen-like atom in an electric field. Literature values obtained with different methods are reproduced. In Sect. 4, the relativistic changes of the Born–Oppenheimer potential curve of H_2^+ are investigated with the help of an *algebraic approximation*. Using extended basis sets, the double perturbation interchange theorems are numerically verified.

2. Theory

2.1. General formalism

We write the one-electron four-component Dirac equation as

$$\{h^D - E\}\psi = \{-2\beta' mc^2 + \boldsymbol{\alpha}\mathbf{p}c + 1(V - E)\}\psi = 0. \tag{2.1}$$

With **1** and **0** being 2 × 2 blocks, we define

$$\beta^0 = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \qquad \beta' = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}, \tag{2.2}$$

so that

$$\beta^0 + \beta' = 1, \qquad \beta^0 - \beta' = \beta. \tag{2.2a}$$

Following Rutkowski [9] we introduce the perturbation parameter ϱ:

$$\{-2\beta' mc^2 + \boldsymbol{\alpha}\boldsymbol{p}c + \beta^0(V - E_\varrho) + \varrho\beta'(V - E_\varrho)\}\psi_\varrho = 0. \tag{2.3}$$

For $\varrho = 1$, (2.3) is the relativistic Dirac equation. For $\varrho = 0$, it corresponds to the nonrelativistic Schrödinger equation for electrons with spin, written as a system of two coupled first-order equations (compare [10, 11]). This can be seen more easily, if (2.3) is written in 2 × 2-block form

$$\begin{bmatrix} V - E_\varrho & \boldsymbol{\alpha}\boldsymbol{p}c \\ \boldsymbol{\alpha}\boldsymbol{p}c & \varrho(V - E_\varrho) - 2mc^2 \end{bmatrix} \begin{bmatrix} \psi_{\varrho+} \\ \psi_{\varrho-} \end{bmatrix} = 0. \tag{2.3a}$$

In conventional relativistic perturbation theory, the four-component description is unitarily transformed into a two-component one, and $1/c$ is used as the perturbation parameter. This often causes insurmountable problems in higher orders since the two-component wavefunction is not analytic in $1/c$ [11, 12]. Note also that the effective mass m/ϱ of the positron states diverges in the nonrelativistic limit $\varrho = 137^2/c^2 \to 0$, i.e. $c \to \infty$. In Rutkowski's approach Eq. (2.3a) [9], the parameter ϱ modifies the potential coupling *and the metric* with respect to the lower component, so that the influence of the positron states disappears in the nonrelativistic limit, and all orders of perturbation theory remain finite and definite.

2.2. Double perturbation theory for relativity and a change in the external potential for many electron systems

The Dirac equation for N particles (electrons), i, with 4^N-component function ψ reads

$$\left\{\sum_i^N [V_i + \boldsymbol{\alpha}_i\boldsymbol{p}_i c - 2\beta_i' m_i c^2] + \sum_{i<j}^N W_{ij} - E\right\}\psi = 0. \tag{2.4}$$

V_i is the external one-particle potential, for instance the electron-nuclear attraction in the case of the Born–Oppenheimer approximation, or an additional field. W_{ij} is the effective two-particle interaction, for instance the "no-pair projected" electron interaction including the Breit terms.

Generalizing the approach of Jankowski and Rutkowski [13], we introduce the many-particle generalizations of β^0 and β' which are needed in the many-particle equivalent of Eq. (2.3):

$$B^0 = \beta_1^0 \cdot \beta_2^0 \cdots \beta_N^0 = \prod_j^N \beta_j^0 \tag{2.5}$$

$$B_i^0 = \beta_1^0 \cdots \beta_{i-1}^0 \beta_{i+1}^0 \cdots \beta_N^0 = \prod_{j \neq i}^N \beta_j^0$$

$$B_{ij}^0 = \prod_{k \neq (i,j)}^N \beta_k^0$$

$$B^1 = \sum_i^N \beta_1^0 \cdots \beta_{i-1}^0 \beta_i' \beta_{i+1}^0 \cdots \sum_i^N B_i^0 \beta_i'$$

$$B_i^1 = \sum_{j \neq i}^N \beta_1^0 \cdots \beta_{i-1}^0 \beta_{i+1}^0 \cdots \beta_{j-1}^0 \beta_j' \beta_{j+1}^0 \cdots \beta_N^0 = \sum_{j \neq i}^N B_{ij}^0 \beta_j'$$

$$B^2 = \sum_{i<j}^N \beta_1^0 \cdots \beta_{i-1}^0 \beta_i' \beta_{i+1}^0 \cdots \beta_{j-1}^0 \beta_j' \beta_{j+1}^0 \cdots \beta_N^0 = \sum_{j>i}^N B_{ij}^0 \beta_i' \beta_j'$$

etc.

$$B^N = \beta_1' \cdot \beta_2' \cdots \beta_N'$$

Furthermore, we expand the one-particle potential as

$$V_i = \sum_p^\infty \gamma^p \cdot V_i^p, \qquad V^p = \sum_i^N V_i^p, \tag{2.6}$$

and the total energy and wavefunction as

$$E = \sum_{r,p} \varrho^r \cdot \gamma^p \cdot E^{p,r}, \qquad \psi = \sum_{r,p} \varrho^r \cdot \gamma^p \cdot \psi^{p,r}. \tag{2.7}$$

We may write the operator of (2.4) by analogy with (2.6) as

$$H - E = \sum_r^N \varrho^r \left(\sum_p^\infty \gamma^p \cdot H^{p,r} - E \cdot B^r \right), \tag{2.8}$$

where

$$H^{0,r} = \sum_i^N (-2\beta_i' mc^2 + \boldsymbol{\alpha}_i \boldsymbol{p}_i c) B_i^r + \sum_i^N V_i^0 \cdot B^r + \sum_{i<j}^N \sum_s^r G_{ij}^{r-s} \cdot B_{ij}^s, \tag{2.9a}$$

$$H^{p,r} = \sum_i V_i^p \cdot B^r \quad \text{for } p > 0. \tag{2.9b}$$

G_{ij} stands for the electromagnetic electron-electron interaction (i.e. Coulomb plus higher order terms). For example $G_{ij}^0 = (1/r_{ij}) \cdot \beta_i^0 \beta_j^0$ is the Coulomb interaction, and

$$G_{ij}^1 = \frac{1}{r_{ij}} \cdot (\beta_i^0 \beta_j' + \beta_i' \beta_j^0) - \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{2r_{ij}} - \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\alpha}_j \cdot \boldsymbol{r}_{ij})}{2r_{ij}^3}$$

is the first order term originating from Coulomb plus Breit interaction.

Combining Eqs. (2.4) to (2.9), we obtain the following hierarchy of equations:

$$(H^{0,0}-E^{0,0}\cdot B^{0})\cdot\psi^{0,0}=0, \tag{2.00}$$

$$\sum_{q=0}^{p}(H^{q,0}-E^{q,0}\cdot B^{0})\cdot\psi^{p-q,0}=0, \tag{2.po}$$

$$\sum_{q,s=0}^{p,r}\left(H^{q,s}-\sum_{t=0}^{s}E^{q,t}\cdot B^{s-t}\right)\cdot\psi^{p-q,r-s}=0. \tag{2.pr}$$

Equation (2.00) is equivalent to the nonrelativistic Schrödinger equation ($\varrho = 0$) with unperturbed potential ($\gamma = 0$). Forming scalar products of Eqs. (2.pr) with $\psi^{0,0}$, and with $\psi^{p',r'}$, and then carrying out a sequence of straightforward manipulations in the sense of the double perturbation interchange concept, we obtain the following expressions for the perturbation energies:

$$E^{1,0}=\langle 00|H^{1,0}|00\rangle \tag{2.10}$$

$$E^{0,1}=\langle 00|H^{0,1}-E^{0,0}\cdot B^{1}|00\rangle \tag{2.01}$$

The second order energies consist of two terms:

$$\begin{aligned}
E^{2,0}&=\langle 00|H^{2,0}|00\rangle+\langle 00|H^{1,0}-E^{1,0}\cdot B^{0}|10\rangle\\
E^{1,1}&=\langle 00|H^{1,1}-E^{1,0}\cdot B^{1}|00\rangle\\
&\quad+2\,\mathrm{Re}\langle 00|H^{1,0}-E^{1,0}\cdot B^{0}|01\rangle\\
&\quad\text{or}\\
&\quad+2\,\mathrm{Re}\langle 00|H^{0,1}-E^{0,1}\cdot B^{0}-E^{0,0}\cdot B^{1}|10\rangle\\
E^{0,2}&=\langle 00|H^{0,2}-E^{0,1}\cdot B^{1}-E^{0,0}\cdot B^{2}|00\rangle\\
&\quad+\langle 00|H^{0,1}-E^{0,1}\cdot B^{0}-E^{0,0}\cdot B^{1}|01\rangle
\end{aligned} \tag{2.11, 2.02}$$

The pure third order energies consist of three terms, and the mixed ones of five terms:

$$\begin{aligned}
E^{3,0}&=\langle 00|H^{3,0}|00\rangle+\langle 00|H^{2,0}-E^{2,0}\cdot B^{0}|10\rangle\\
&\quad+\langle 00|H^{1,0}-E^{1,0}\cdot B^{0}|20\rangle\\
&\text{or}\\
&=\langle 00|H^{3,0}|00\rangle+2\,\mathrm{Re}\langle 00|H^{2,0}-E^{2,0}\cdot B^{0}|10\rangle\\
&\quad+\langle 10|H^{1,0}-E^{1,0}\cdot B^{0}|10\rangle\\
E^{2,1}&=\langle 00|H^{2,1}-E^{2,0}\cdot B^{1}|00\rangle\\
&\quad+\langle 00|H^{2,0}-E^{2,0}\cdot B^{0}|01\rangle\\
&\quad+\langle 00|H^{1,1}-E^{1,1}\cdot B^{0}-E^{1,0}\cdot B^{1}|10\rangle\\
&\quad+\langle 00|H^{1,0}-E^{1,0}\cdot B^{0}|11\rangle,\\
&\quad+\langle 00|H^{0,1}-E^{0,1}\cdot B^{0}-E^{0,0}\cdot B^{1}|20\rangle
\end{aligned} \tag{2.30}$$

$$
\begin{aligned}
&\text{or}\\
&= \langle 00|H^{2,1} - E^{2,0} \cdot B^{1}|00\rangle\\
&\quad + 2\,\mathrm{Re}\langle 00|H^{2,0} - E^{2,0} \,.\, B^{0}|01\rangle\\
&\quad + 2\,\mathrm{Re}\langle 00|H^{1,1} - E^{1,1} \cdot B^{0} - E^{1,0} \cdot B^{1}|10\rangle\\
&\quad + 2\,\mathrm{Re}\langle 10|H^{1,0} - E^{1,0} \cdot B^{0}|01\rangle\\
&\quad + \langle 10|H^{0,1} - E^{0,1} \cdot B^{0} - E^{0,0} \cdot B^{1}|10\rangle
\end{aligned}
\tag{2.21}
$$

$$
\begin{aligned}
E^{1,2} &= \langle 00|H^{1,2} - E^{1,1} \cdot B^{1} - E^{1,0} \cdot B^{2}|00\rangle\\
&\quad + \langle 00|H^{1,1} - E^{1,1} \cdot B^{0} - E^{1,0} \cdot B^{1}|01\rangle\\
&\quad + \langle 00|H^{0,2} - E^{0,2} \cdot B^{0} + E^{0,1} \cdot B^{1} - E^{0,0} \cdot B^{2}|10\rangle\\
&\quad + \langle 00|H^{0,1} - E^{0,1} \cdot B^{0} - E^{0,0} \cdot B^{1}|11\rangle\\
&\quad + \langle 00|H^{1,0} - E^{1,0} \cdot B^{0}|02\rangle\\
&\text{or}\\
&= \langle 00|H^{1,2} - E^{1,1} \cdot B^{1} - E^{1,0} \cdot B^{2}|00\rangle\\
&\quad + 2\,\mathrm{Re}\langle 00|H^{0,2} - E^{0,2} \cdot B^{0} - E^{0,1} \cdot B^{1} - E^{0,0} \cdot B^{2}|10\rangle\\
&\quad + 2\,\mathrm{Re}\langle 00|H^{1,1} - E^{1,1} \cdot B^{0} - E^{1.0} \cdot B^{1}|01\rangle\\
&\quad + 2\,\mathrm{Re}\langle 01|H^{0,1} - E^{0,1} \cdot B^{0} - E^{0,0} \cdot B^{1}|10\rangle\\
&\quad + \langle 01|H^{1,0} - E^{1,0} \cdot B^{0}|01\rangle
\end{aligned}
\tag{2.12}
$$

$$
\begin{aligned}
E^{0,3} &= \langle 00|H^{0,3} - E^{0,2} \cdot B^{1} - E^{0,1} \cdot B^{2} - E^{0,0} \cdot B^{3}|00\rangle\\
&\quad + 2\,\mathrm{Re}\langle 00|H^{0,2} - E^{0,2} \cdot B^{0} - E^{0,1} \cdot B^{1} - E^{0,0} \cdot B^{2}|01\rangle\\
&\quad + \langle 01|H^{0,1} - E^{0,1} \cdot B^{0} - E^{0,0} \cdot B^{1}|01\rangle
\end{aligned}
\tag{2.03}
$$

The higher order energies are even more complicated:

$$
\begin{aligned}
E^{3,1} &= \langle 00|H^{3,1} - E^{3,0} \cdot B^{1}|00\rangle\\
&\quad + 2\,\mathrm{Re}\langle 00|H^{3,0} - E^{3,0} \cdot B^{0}|01\rangle\\
&\quad + 2\,\mathrm{Re}\langle 00|H^{2,1} - E^{2,1} \cdot B^{0} - E^{2,0} \cdot B^{1}|10\rangle\\
&\quad + 2\,\mathrm{Re}\langle 01|H^{2,0} - E^{2,0} \cdot B^{0}|10\rangle\\
&\quad + \langle 10|H^{1,1} - E^{1,1} \cdot B^{0} - E^{1,0} \cdot B^{1}|10\rangle\\
&\quad + 2\,\mathrm{Re}\{\langle 10|H^{1,0} - E^{1,0} \cdot B^{0}|11\rangle\\
&\qquad\quad + \langle 00|H^{2,0} - E^{2,0} \cdot B^{0}|11\rangle\}\\
&\quad\text{or}\\
&\quad + 2\,\mathrm{Re}\{\langle 00|H^{1,1} - E^{1,1} \cdot B^{0} - E^{1,0} \cdot B^{1}|20\rangle\\
&\qquad\quad + \langle 10|H^{0,1} - E^{0,1} \cdot B^{0} - E^{0,0} \cdot B^{1}|20\rangle\\
&\qquad\quad + \langle 01|H^{1,0} - E^{1,0} \cdot B^{0}|20\rangle\}
\end{aligned}
\tag{2.31}
$$

$$
\begin{aligned}
E^{2,2} = {} & \langle 00|H^{2,2} - E^{2,1}\cdot B^{1} - E^{2,0}\cdot B^{2}|00\rangle \\
& + 2\,\mathrm{Re}\langle 00|H^{2,1} - E^{2,1}\cdot B^{0} - E^{2,0}\cdot B^{1}|01\rangle \\
& + 2\,\mathrm{Re}\langle 00|H^{1,2} - E^{1,2}\cdot B^{0} - E^{1,1}\cdot B^{1} - E^{1,0}\cdot B^{2}|10\rangle \\
& + 2\,\mathrm{Re}\langle 01|H^{1,1} - E^{1,1}\cdot B^{0} - E^{1,0}\cdot B^{1}|10\rangle \\
& + \langle 01|H^{2,0} - E^{2,0}\cdot B^{0}|01\rangle \\
& + \langle 10|H^{0,2} - E^{0,2}\cdot B^{0} - E^{0,1}\cdot B^{1} - E^{0,0}\cdot B^{2}|10\rangle \\
& + \langle 11|H^{0,0} - E^{0,0}\cdot B^{0}|11\rangle \\
& + 2\,\mathrm{Re}\{\langle 01|H^{0,1} - E^{0,1}\cdot B^{0} - E^{0,0}\cdot B^{1}|20\rangle \\
& \qquad + \langle 00|H^{0,2} - E^{0,2}\cdot B^{0} - E^{0,1}\cdot B^{1} - E^{0,0}\cdot B^{2}|20\rangle\} \\
& \textbf{or} \\
& + 2\,\mathrm{Re}\{\langle 10|H^{1,0} - E^{1,0}\cdot B^{0}|02\rangle \\
& \qquad + \langle 00|H^{2,0} - E^{2,0}\cdot B^{0}|02\rangle\} \qquad (2.22)
\end{aligned}
$$

etc.

Up to third order, i.e. for $E^{3,0}$, $E^{2,1}$, $E^{1,2}$ $E^{0,3}$, first order functions are sufficient, whereas for $E^{3,1}$, $\psi^{2,0}$ or $\psi^{1,1}$; and for $E^{2,2}$, $\psi^{1,1}$, $\psi^{2,0}$ or $\psi^{1,1}$, $\psi^{0,2}$ are needed, respectively. Further equivalent expressions can be derived for the third and higher order energies which are however simpler than the ones given.

For numerical calculations it is more convenient to work with the upper component functions only. The corresponding expressions, which were obtained by a tedious elimination process, are given in the Appendix. We note that no divergencies arise in the present approach.

3. First application using an analytic approach: relativistic stark effect of hydrogenlike ions

3.1. Perturbation energy

A simple example for the application of these formulae is the relativistic correction to the electric polarizability of hydrogen-like atoms, which can be solved by purely analytic methods. The appropriate Hamiltonians, as defined in Eq. (2.9), are given in atomic units by

$$H^{0,0} = -2\beta' c^{2} + \boldsymbol{\alpha} pc - \beta^{0}\cdot Z/r, \qquad E^{0,0}B^{0} = -\beta^{0}\cdot Z^{2}/2, \tag{3.1a}$$

$$H^{0,1} = -\beta'\cdot Z/r, \qquad E^{0,0}B^{1} = -\beta'\cdot Z^{2}/2, \tag{3.1b}$$

$$H^{1,0} = \beta^{0}\cdot F\cdot z, \qquad H^{1,1} = \beta'\cdot F\cdot z, \tag{3.1c}$$

where Z is the nuclear charge, and F is the external field strength in the direction of coordinate z. The well-known nonrelativistic polarizability α is

$$\alpha = -2E^{2,0} = 4.5/Z^{4}. \tag{3.2}$$

The lowest order relativistic correction, according to Eq. (1.6), is

$$\Delta^{\mathrm{rel}}\alpha = -2E^{2,1}. \tag{3.3}$$

We evaluate $E^{2,1}$ as given in Eqs. (2.21, A.21, B.21), so we need

$$\varphi_{+}^{0,0} = \sqrt{4Z^3} \cdot e^{-Zr} \cdot s_{1/2}, \tag{3.4a}$$

$$\varphi_{-}^{0,0} = -i\sqrt{Z^5}/c \cdot e^{-Zr} \cdot p_{1/2}, \tag{3.4b}$$

$$\varphi_{+}^{0,1} = -\sqrt{Z^7}/c^2 \cdot \ln r \cdot e^{-Zr} \cdot s_{1/2}, \tag{3.4c}$$

and

$$\varphi_{+}^{1,0} = -\sqrt{4/3Z^3} \cdot r^2 \cdot (Z/r + Z^2/2)(\sqrt{2/3}p_{3/2} - \sqrt{1/3}p_{1/2}) \cdot e^{-Zr}, \tag{3.5a}$$

$$\begin{aligned}\varphi_{-}^{1,0} = -i/\sqrt{Zc^2} \cdot r^2 \cdot \{&(Z^2/6 - Z/3r - 1/r^2) \cdot s_{1/2} \\ &-\sqrt{2}(Z^2/6 + Z/6r) \cdot d_{3/2}\} \cdot e^{-Zr}\end{aligned} \tag{3.5b}$$

[9, 14]. The final result of the analytical integrations of (A.21) is

$$\begin{aligned}E^{2,1} &= \langle \varphi_{-}^{00} | 9/4Z^4 | \varphi_{-}^{00} \rangle \\ &\quad + 2\langle \varphi_{+}^{00} | 9/4Z^4 | \varphi_{+}^{01} \rangle \\ &\quad + 2\langle \varphi_{-}^{00} | z | \varphi_{-}^{10} \rangle \\ &\quad + 2\langle \varphi_{+}^{10} | z | \varphi_{+}^{01} \rangle \\ &\quad + \{\langle \varphi_{-}^{10} | -Z/r + Z^2/2 | \varphi_{-}^{10} \rangle + \langle \varphi_{+}^{10} | Z^4/8c^2 | \varphi_{+}^{10} \rangle\} \\ &= \left(\frac{9}{16} + \frac{25}{16} - \frac{3}{8} - \frac{17}{192} + \frac{43}{64}\right) \Big/ Z^2c^2 \\ &= 7/(3Z^2c^2).\end{aligned} \tag{3.6}$$

This yields to first order

$$\Delta^{\mathrm{rel}}\alpha = -14/(3Z^2c^2). \tag{3.7}$$

The relative relativistic correction to first order,

$$\delta^{\mathrm{rel}}\alpha = -(28/27) \cdot (Z/c)^2, \tag{3.8}$$

depends on $(Z/c)^2$, as do the relative relativistic corrections of most expectation values.

Equations (3.7, 8) have already been obtained by other authors [15–20], using different approaches.

3.2. Perturbation function

The next higher relativistic term is $E^{2,2}$. According to Eq. (2.22), the lowest order mixed perturbation function $\varphi^{1,1}$ is needed in addition to the nonrelativistic function $\varphi^{2,0}$. We will here derive an explicit expression for $\varphi^{1,1}$. The explicit equation reads

$$\begin{bmatrix} Z^2/2 - Z/r & \alpha pc \\ \alpha pc & -2c^2 \end{bmatrix} \begin{bmatrix} \varphi_+^{1,1} \\ \varphi_-^{1,1} \end{bmatrix}$$

$$= -\begin{bmatrix} 0 & 0 \\ 0 & z \end{bmatrix} \begin{bmatrix} \varphi_+^{0,0} \\ \varphi_-^{0,0} \end{bmatrix} - \begin{bmatrix} z & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \varphi_+^{0,1} \\ \varphi_-^{0,1} \end{bmatrix} - \begin{bmatrix} Z^4/8c^2 & 0 \\ 0 & Z^2/2 - Z/r \end{bmatrix} \begin{bmatrix} \varphi_+^{1,0} \\ \varphi_-^{1,0} \end{bmatrix}. \tag{3.9}$$

Inserting (3.4) and (3.5) and eliminating $\varphi_-^{1,1}$ leads to

$$\begin{aligned} &(p^2/2 - Z/r + Z^2/2)\varphi_+^{1,1} \\ &\quad = 1/c^2\sqrt{12Z}\{-\sqrt{2}(Z^3 - Z^2/2r - Z/r^2)\,e^{-Zr} \cdot (\sqrt{1/3} \cdot p_{3/2} + \sqrt{2/3} \cdot p_{1/2}) \\ &\qquad + (3Z^4 r - 7Z^3/2 - 2Z^2/r - Z/r^2 + 2Z^2 r \ln r)\,e^{-Zr} \\ &\qquad \times (\sqrt{2/3} \cdot p_{3/2} - \sqrt{1/3} \cdot p_{1/2})\}. \end{aligned} \tag{3.10}$$

Subsituting

$$\begin{aligned} \varphi_+^{1,1} = \sqrt{Z^3/12c^4} \cdot r \cdot e^{-Zr}\{&-f_1(2Zr) \cdot \sqrt{2}[\sqrt{1/3} \cdot p_{3/2} + \sqrt{2/3} \cdot p_{1/2}] \\ &+ f_2(2Zr) \cdot [\sqrt{2/3} \cdot p_{3/2} - \sqrt{1/3} \cdot p_{1/2}]\} \end{aligned} \tag{3.11}$$

yields the following equation for f_i:

$$(x \cdot d^2/dx^2 + (4 - x) \cdot d/dx - 1)f_i = -\varphi_i \tag{3.12}$$

with

$$\varphi_1 = 1 - 1/x - 4/x^2, \tag{3.13}$$

$$\varphi_2 = 1.5x - 3.5 - 4/x - 4/x^2 + x \cdot \ln(x/2Z) \tag{3.14}$$

where $x = 2Zr$. Taking into account that the differential equation for the Laguerre polynomials reads

$$(x \cdot d^2/dx^2 + (k + 1 - x) \cdot d/dx + n)L_n^k = 0, \tag{3.15}$$

we note that the polynomials L_n^3 are the eigenfunctions of the operator on the left hand side of Eq. (3.12):

$$(x \cdot d^2/dx^2 + (4 - x) \cdot d/dx - 1)L_n^3 = -(n + 1)L_n^3. \tag{3.16}$$

Therefore it is natural to expand f_i and φ_i in terms of these polynomials:

$$\varphi_i = \sum_{n=0}^{\infty} c_n^{(i)} \cdot L_n^3, \tag{3.17}$$

$$f_i = \sum_{n=0}^{\infty} c_n^{(i)}/(n + 1) \cdot L_n^3. \tag{3.18}$$

The expansion coefficients $c_n^{(i)}$ can be obtained with the help of the generating function W,

$$W(x, t) = e^{-xt/(1-t)}/(1 - t)^4, \tag{3.19}$$

namely:

$$\sum_{n=0}^{\infty} c_n^{(i)} \cdot (n+3)!/n! \cdot t^n = \int_0^{\infty} dx \cdot x^3 \cdot e^{-x} \cdot W(x,t) \cdot \varphi_i(x). \tag{3.20}$$

The evaluation of the integral yields

$$c_0^{(1)} = 0, \qquad c_n^{(1)} = -2 \cdot (2n+3) \cdot n!/(n+3)! \quad \text{for } n > 0; \tag{3.21}$$

$$c_0^{(2)} = 53/6 - 4\delta, \qquad c_1^{(2)} = -21/4 + \delta, \quad \delta = \ln 2Z + \gamma,$$

$$c_n^{(2)} = -4 \cdot [(n-1) \cdot n \cdot (n+3) - 6] \cdot (n-2)!/(n+3)! \quad \text{for } n > 1. \tag{3.22}$$

Here γ is the Euler constant, $\gamma = 0.577\ 215\ 664\ \ldots$.

We are now in the position to calculate the norm of the perturbation function $\varphi^{1,1}$:

$$\langle \varphi^{1,1} | \varphi^{1,1} \rangle = 2I_1 + I_2 \tag{3.23}$$

with

$$I_i = 1/(24Z^2(2c)^4) \cdot \sum_{n=0}^{\infty} c_n^{(i)} \cdot (n+3) \cdot [c_n^{(i)} \cdot (n+2)^2/(n+1) - c_{n+1}^{(i)} \cdot (n+4)]. \tag{3.24}$$

The evaluation of the sum yields

$$\begin{aligned} I_1 &= 1/(96Z^2c^4) \cdot \sum_{n=1}^{\infty} (2n+3)(7n^2+8n+7)/(n+1)^3(n+2)^2(n+3) \\ &\approx 3.3614 \times 10^{-3}/Z^2c^4 \end{aligned} \tag{3.25}$$

$$\begin{aligned} I_2 &= 1/(384Z^2c^4) \cdot \{47399/24 - \delta \cdot 4177/3 + 258 \cdot \delta^2 \\ &\quad + \sum_{n=2}^{\infty} 16(n^4 + 6n^3 + n^2 - 32n - 30)(n(n-1)(n+3) - 6)(n-2)!^2 \\ &\quad \div (n+3)!(n+2)!(n+1)\} \\ &\approx (5.14312 - 3.62587\delta - 0.67188\delta^2)/(Z^2c^4). \end{aligned} \tag{3.26}$$

The use of the present technique in the solution of the higher order perturbation equations and in the evaluation of the appropriate mixed perturbation energies will be presented in a subsequent paper [21]. We here present just the final result for the relative second order relativistic correction:

$$\delta^{2\cdot\mathrm{rel}}\alpha = -0.1175 \cdot (Z/c)^4 \tag{3.27}$$

4. Second application using an algebraic approach: relativistic change of the H_2^+ potential curve

4.1. Perturbations energies

The formulae of the Appendix and Eq. (1.12) have been used to investigate the relativistic changes of the Born–Oppenheimer potential curve of H_2^+. Using an optimized floating Gaussian lobe basis set of 27 functions, we obtained the numerical results given in Table 1.

Rather large basis sets are needed to obtain good numerical agreement between the different expression for the mixed perturbation energies (compare the data for $E^{1,1}$, $E^{2,1}$ and $E^{1,2}$ in Table 1). The same is also true in the framework of the relativistic pseudopotential approach [28]. We note that the numerical problems with the double perturbation interchange theorem are similar to those in a number of other situations: the Hellmann–Feynman theorem, the calculation of dipole transition moments by the length and velocity formulae, the calculation of dia- and paramagnetic contributions to magnetic properties, and the determination of nonadiabatic coupling elements.

With regards to the force constant, we note the significant relativistic increase (see $E^{2,1}$ and $\delta^1 k$ in the table; previous literature values do not agree well with the present ones). One may speculate that δk is in general of the order of $10 \cdot (Z/c)^2$, thus becoming qualitatively important for heavier systems. In the future we shall investigate in more detail the physical origin of the empirical result that the relativistic *increase* in force constants is frequent and large [3], even in cases where the bond energy is relativistically decreased [29, 30].

With regards to the bond length, the leading relativistic correction is $\Delta^1 R = -0.5 E^{1,1}/E^{2,0}$. As has been discussed in some detail by Schwarz [1, 8], $E^{1,1}$ should be positive in most cases, so that $\Delta^1 R$ is usually negative (relativistic bond length contraction). According to Eq. (1.12), $E^{1,2}$, $E^{2,1}$ and $E^{3,0}$ contribute to the second order relativistic bond length change $\Delta^2 R$. The most significant term is the one proportional to $E^{1,1} \cdot E^{2,1}/(E^{2,0})^2$. That is, the relativistic change of the force constant ($E^{2,1}$) is more important than both the change of the

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

	This work	Some literature values
R_e^{nr}	1.997192	1.997193 [22]; 1.9972 [25]
$E^{0,0}$	-0.6026343	-0.6026342 [22, 23, 24]
$E^{1,0}$	0	
$E^{0,1} \cdot c^2$	-0.138531 (-0.138330)[a]	-0.13832 [22, 23];[a] -0.13828 [24];[a] -0.1386 [27][a]
$E^{2,0}$	0.0514503	0.0515 [22]; 0.05141 [25]
$E^{1,1} \cdot c^2$	0.07175 ± 0.00003	0.076 [27]
$E^{0,2} \cdot c^4$	-0.0403942	-0.0399 [24];[a] -0.0417 [23]
$E^{3,0}$	-0.0436321	-0.057 [25]
$E^{2,1} \cdot c^2$	0.70218 ± 0.00003	0.4 [22]; -0.06 [27]
$E^{1,2} \cdot c^4$	-0.0024 ± 0.0001	
$E^{0,3} \cdot c^6$	-0.0278344	-0.0283 [24];[a] -0.0286 [23]
k^{nr}	0.1029	0.1028 [25]; 0.1030 [22]; 0.10307 [26]
$\delta^1 k \cdot c^2$	$+13.648$	8 [22]; -1 [26]
$\Delta^1 R \cdot c^2$	-0.6965	-0.706 [22]; -0.6 [26]
$\Delta^2 R/\Delta^1 R \cdot c^2$	-14.6	
$\Delta DE \cdot c^2$	-0.01352	-0.0133 [22, 23]

[a] These values refer to $R = 2$; our results corroborate [22–24], but not [27]

nonrelativistic force constant with internuclear distance (nonrelativistic anharmonicity, $E^{3,0}$), and the second order relativistic change of the slope of the potential curve, $E^{1,2}$ (compare Eq. 1.12):

$$\begin{array}{cccc} (-E^{1,1}/2E^{2,0}) & (-E^{2,1}/E^{2,0}) & (E^{1,2}/E^{1,1}) & (3E^{3,0}E^{1,1}/4E^{2,0}E^{2,0}) \\ \downarrow & \downarrow & \downarrow & \downarrow \\ \Delta R \approx -0.697\lambda \cdot (1 & -13.65\lambda & -0.034\lambda & -0.887\lambda). \end{array} \tag{4.1}$$

It will be interesting to investigate whether this finding on H_2^+ ($\lambda = 1/c^2$) can be generalized to other molecules. In any case, one gets the impression that for higher nuclear charges, where $\lambda = Z^2/c^2$ is no longer small compared with 1, the second order relativistic term $E^{1,2}$ may become of qualitative importance in addition to $E^{2,1}$. Even the second order relativistic change of the force constant, $E^{2,2}$, which is a fourth-order perturbation energy that corrects $E^{2,1}$, may turn out to be necessary in order to understand ΔR qualitatively for large Z values.

4.2. *Interchange relations*

In order to understand the lowest order relativistic bond length change,

$$\Delta R \approx -(dE^{\mathrm{rel}}/dR)/k^{\mathrm{rel}} \tag{4.2}$$

in *physical* terms, we need to understand the two terms $(dE^{\mathrm{rel}}/dR) \approx E^{1,1}$, and k^{rel}. According to Eq. (A.11) we may express $E^{1,1}$ in two different ways:

$$E^{1,1} = \langle \varphi_+^{00} | \boldsymbol{\sigma p} \cdot \partial V/\partial R \cdot \boldsymbol{\sigma p} | \varphi_+^{00} \rangle / 4c^2 + \langle \varphi_+^{00} | \partial V/\partial R | 2\varphi_+^{01} \rangle \tag{4.3}$$

or

$$\begin{aligned} E^{1,1} = {} & \langle \varphi_+^{00} | \boldsymbol{\sigma p} \cdot \partial V/\partial R \cdot \boldsymbol{\sigma p} | \varphi_+^{00} \rangle / 4c^2 \\ & + \langle \varphi_+^{00} | \boldsymbol{\sigma p} \cdot V \cdot \boldsymbol{\sigma p} - E^{0,0} \cdot p^2 - 2c^2 E^{0,1} | 2\, \partial \varphi_+^{00} / \partial R \rangle / 2c^2 \end{aligned} \tag{4.4}$$

Here, only upper two-component spinors have been used, so that there is some similarity to the Pauli approach. The first term in both Eq. (4.3) and Eq. (4.4) is the expectation value of the bond length change of Rutkowski's relativistic first order operator. At $R = R_e$

$$\boldsymbol{\sigma p} \cdot \partial V/\partial R \cdot \boldsymbol{\sigma p} = \partial/\partial R \cdot (\boldsymbol{\sigma p}[V - E]\boldsymbol{\sigma p}]. \tag{4.5}$$

As has recently been explained by Schwarz ([1], Sect. III.1.1.B), this term should, in general, be negative in the Pauli approach, i.e. *bond expanding*. This is because the repulsive Darwin potential becomes more important for shorter bond lengths as the electron density of bonding orbitals is in general higher between the nuclei than on the "backside" of the atoms. Indeed, we obtain in the present case

$$\langle \partial(\boldsymbol{\sigma p} V \boldsymbol{\sigma p})/4\, \partial R \rangle = -0.09225 \tag{4.6}$$

In the quasirelativistic pseudopotential approach, the corresponding term is often negative too (Collignon [28]), while in the Dirac approach $\partial^2 H^D/\partial R\, \partial c$ is zero (for details see [1, 8]).

If we prefer scheme (4.3), we have to add to (4.6) the *Hellmann–Feynman-force*, $\partial V/\partial R$, exerted by the upper component's contribution of the *relativistic first order density change*, $2 \cdot \varphi^{00}_{+} \cdot \varphi^{01}_{+}$. Relativistic molecular orbital contraction will in most caases cause bond length contraction [1, 8]. Indeed, we obtain in the present case

$$\langle \varphi^{00}_{+} | \partial V/\partial R | \varphi^{01}_{+} \rangle \cdot 2c^2 = +0.16402 \tag{4.7}$$

So, in scheme (4.3) a total bond length contraction results because the bond-contracting Hellmann-Feynman force of the relativistically contracted charge distribution, $2 \cdot \varphi^{00}_{+} \cdot \varphi^{01}$, overweights the bond expanding action of the relativistic modification of the force operator, $\boldsymbol{\sigma p}(\partial V/\partial R)\boldsymbol{\sigma p}/4c^2$. The latter term is related to the fact that the electron's position of charge and position of mass are different observables and are represented by non-communting operators [6, 31].

Snijders and Pykkö [32] have advocated using the alternative scheme (4.4). There we need three additional terms, obtained form the bond length change of the density,

$$\varrho' = \partial \varrho/\partial R \approx 2 \cdot \varphi^{00}_{+} \cdot \partial \varphi^{00}_{+}/\partial R = 2 \cdot \varphi^{0,0}_{+} \cdot \varphi^{1,0}_{+}. \tag{4.8}$$

The first contribution to the second term of Eq. (4.4) is large and positive, as to be expected, but is strongly "renormalized" with respect to the energy by the other two contributions:

$$\left.\begin{array}{r} \langle \varrho' | \boldsymbol{\sigma p} V \boldsymbol{\sigma p}/4 \rangle = +0.57711 \quad (4.9) \\ -E^{00} \langle \varrho' | p^2/4 \rangle = -0.26116 \quad (4.10) \\ -c^2 E^{01} \langle \varrho' | 1 \rangle = -0.15198 \quad (4.11) \end{array}\right\} = +0.16397$$

The 0.03% difference between the value of (4.7) and the sum of (4.9) to (4.11) is due to basis set truncation. We have the general experience that the double perturbation interchange relations are numerically very sensitive.

Summarizing, $E^{1,1}$ is a sum of terms with different signs, the sign and magnitude of its total value being physically more or less evident, depending on whether scheme (4.3) or (4.4) in chosen. The validity of the relativistic double perturbation interchange theorem has been numerically verified for the first time.

Finally, we discuss the third order term $E^{2,1}$, determining $\Delta^{\mathrm{rel}}k$ to first order and, thereby, $\Delta^{\mathrm{rel}}R$ to second order. Assuming that we have physically understood the value of the nonrelativistic force constant

$$k^{\mathrm{nrel}} = 2E^{2,0} = +0.60709 - 0.50418 = 0.10290, \tag{4.12}$$

which is also a difference of two opposing contributions, we would like to *understand* its rather large relativistic correction

$$\Delta^{\mathrm{rel}}k \approx 2E^{2,1}. \tag{4.13}$$

However, this goal seems hardly achievable, since $E^{2,1}$ consists of many rather large terms of different sign. This holds both for the straight forward perturbation expression, symbolically written as

$$\begin{aligned} E^{2,1} &= \langle 00|21|00\rangle + \langle 00|20|01\rangle + \langle\langle 00|11|10\rangle + \langle 00|10|11\rangle + \langle 00|01|20\rangle \\ &= 0.090 \qquad + 1.609 \qquad + 0.129 \qquad - 2.144 \qquad + 1.018 \\ &= 0.702 \end{aligned} \tag{4.14}$$

and also, if we eliminate the second order functions $|11\rangle$ and $|20\rangle$,

$$\begin{aligned} E^{2,1} &= \langle 00|21|00\rangle + 2\langle 00|20|01\rangle + 2\langle 00|11|10\rangle + 2\langle 10|10|01\rangle + \langle 10|01|10\rangle \\ &= 0.090 \qquad + 3.219 \qquad + 0.257 \qquad - 1.183 \qquad - 1.681 \\ &= 0.702 \end{aligned} \tag{4.15}$$

Here the central symbols $|ij|$ stand for H^{ij} minus the $E \cdot B$ terms, as given in Eq. (2.21).

5. Summary

In order to investigate relativistic corrections of chemically interesting observables, at least third order perturbation theory is needed. Using Rutkowski's convergent relativistic perturbation approach, the appropriate double perturbation formulae have been developed. The expressions are given in terms of four-component wavefunctions in Sect. 2, in terms of the upper two-component functions in Appendix A, and in terms of two-component orbitals within the framework of the single particle approximation in Appendix B.

The formalism has first been tested analytically for the case of the relativistic correction of the electric dipole polarizability of hydrogen-like ions (Sect. 3). The perturbation functions up to second order, including $\varphi^{1,1}$, are given. $\varphi^{1,1}$ is normalizable, as it should be. The perturbation energies $E^{2,1}$ and $E^{2,2}$ are consistent with results from the literature obtained in different ways. Finally the formalism has been applied to H_2^+ in a Gaussian basis (Sect. 4), using variation perturbation theory as developed by Rutkowski and Rutkowska [24].

There are two general goals, namely to calculate numerical values, and to understand their physical origin. While the first goal has been achieved, the second goal seems only achievable for first and second order effects.

If we are interested in relativistic changes of structural parameters we first need $E^{1,1}$ of Eq. (1.12) which is, however, even qualitatively only sufficient for light systems. Only one of the first order densities is needed, either $\varrho^{01} \approx 2\,\mathrm{Re}\,\psi^{00} \cdot \psi^{01}$ or $\varrho^{10} \approx 2\,\mathrm{Re}\,\psi^{00} \cdot \psi^{10}$ (see Eqs. 2.11, A.11). The formal analysis of $E^{1,1}$ [8] has already made evident that a physical understanding cannot be gained without the detailed analysis of numerical results on typical molecular examples. This holds even more for the perturbation energies $E^{2,1}$ and $E^{1,2}$, where both ϱ^{01} *and* ϱ^{10} and *also* second order densities are needed. However, by introducing interchange relations, one can get by with first order wavefunctions only. The interchange relations have been verified numerically to high accuracy.

The most important higher order term in the present context is $E^{2,1}$, the first-order relativistic change of force constant. For heavy systems, $E^{1,2}$ (relativistic second-order change of slope of the potential curve), $E^{3,0}$ (anharmonicity) and $E^{2,2}$ (relativistic second-order change of force constant) are also needed for a qualitative understanding of the relativistic changes of molecular structure.

Reliable numerical results for many-electron systems can only be obtained, if electron interaction is also treated appropriately. In order to "understand" the influence of correlation on the relativistic changes of chemical properties, triple perturbation theory is needed. Preliminary results, which are not reported here, do not look very promising if simple explanations are looked for.

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Appendix

A. Reformulation in terms of the upper two-component functions

In the following, the bras and kets refer only to the 2^N upper components with respect to all electrons of the N-electron Dirac wavefunction.

$$E^{0,1} = \langle 00|R^{0,1} + T^1|00\rangle \tag{A.01}$$

$$E^{1,0} = \langle 00|V^1|00\rangle \tag{A.10}$$

$$E^{2,0} = \langle 00|V^2|00\rangle + \langle 00|V^1 - E^{1,0}|10\rangle \tag{A.20}$$

$$\begin{aligned} E^{1,1} = {} & \langle 00|R^{1,1}|00\rangle \\ & +2\,\mathrm{Re}\langle 00|V^1 - E^{1,0}|01\rangle \qquad \text{(A.11)} \\ & \textbf{or} \\ & +2\,\mathrm{Re}\langle 00|R^{0,1} + T^1 - E^{0,1}|10\rangle \end{aligned}$$

$$\begin{aligned} E^{0,2} = {} & \langle 00|R^{0,2} + P^{0,2} + Q^{0,2} + 3T^2 - T^{0,1}E^{0,1}|00\rangle \\ & + \langle 00|R^{0,1} + T^1 - E^{0,1}|01\rangle \end{aligned} \tag{A.02}$$

$$\begin{aligned} E^{3,0} = {} & \langle 00|V^3|00\rangle + \langle 10|V^1 - E^{1,0}|10\rangle \\ & + 2\,\mathrm{Re}\langle 00|V^2 - E^{2,0}|10\rangle \end{aligned} \tag{A.30}$$

$$\begin{aligned} E^{2,1} = {} & \langle 00|R^{2,1}|00\rangle \\ & + 2\,\mathrm{Re}\langle 00|V^2 - E^{2,0}|01\rangle + 2\,\mathrm{Re}\langle 00|R^{1,1} - E^{1,1}|10\rangle \\ & + 2\,\mathrm{Re}\langle 10|V^1 - E^{1,0}|01\rangle + \langle 10|R^{0,1} + T^1 - E^{0,1}|10\rangle \end{aligned} \tag{A.21}$$

$$\begin{aligned} E^{1,2} = {} & \langle 10|S^{1,2}+P^{1,2}+Q^{1,2}-T^{0,1}E^{1,1}|00\rangle \\ & +2\,\mathrm{Re}\langle 00|R^{1,1}-E^{1,1}|01\rangle \\ & +2\,\mathrm{Re}\langle 00|R^{0,2}+P^{0,2}+Q^{0,2}+3T^2-T^{0,1}E^{0,1}-E^{0,2}|10\rangle \\ & +2\,\mathrm{Re}\langle 01|R^{0,1}+T^1-E^{0,1}|10\rangle \\ & +\langle 01|V^1-E^{1,0}|01\rangle. \end{aligned} \tag{A.12}$$

Here the following abbreviations are used

$$T^{0,1}=\sum_{i}^{N} p_i^2/4m^2c^2 \tag{A.1}$$

$$T^1=\sum_{i\neq j}^{N} p_i^2p_j^2/8m^3c^2 \tag{A.2}$$

$$T^2=\sum_{i\neq j\neq k}^{N} p_i^2p_j^2p_k^2/64m^5c^4 \tag{A.3}$$

$$R^{pr}=\sum_{i}^{N} \boldsymbol{\sigma}_i\boldsymbol{p}_i(V^p-E^{p,0})^r\boldsymbol{\sigma}_i\boldsymbol{p}_i/2m(2mc^2)^r \tag{A.4}$$

$$P^{p,2}=\sum_{i\neq j}^{N} (p_j^2\cdot\boldsymbol{\sigma}_i\boldsymbol{p}_i(V^p-E^{p,0})\boldsymbol{\sigma}_i\boldsymbol{p}_i+\boldsymbol{\sigma}_i\boldsymbol{p}_i(V^p-E^{p,0})\boldsymbol{\sigma}_i\boldsymbol{p}_i\cdot p_j^2)/16m^3c^4 \tag{A.5}$$

$$Q^{p,2}=\sum_{i\neq j}^{N} (\boldsymbol{\sigma}_j\boldsymbol{p}_j\cdot\boldsymbol{\sigma}_i\boldsymbol{p}_i(V^p-E^{p,0})\boldsymbol{\sigma}_i\boldsymbol{p}_i\cdot\boldsymbol{\sigma}_j\boldsymbol{p}_j)/32m^3c^4 \tag{A.6}$$

$$S^{1,2}=\sum_{i}^{N} \boldsymbol{\sigma}_i\boldsymbol{p}_i[(V^1-E^{1,0})(V^0-E^{0,0})]\boldsymbol{\sigma}_i\boldsymbol{p}_i/4m^5c^4. \tag{A.7}$$

Since coincident indices do not appear in Eqs. (A.2), (A.3), (A.5), (A.6), no divergent terms arise, contrary to the Pauli–Foldy–Wouthuysen approach [11, 12].

B. Independent particle approximation

The 2^N-component function of Sect. 3 is now approximated by a Slater determinant of upper 2-component spinors φ_{+i}

$$|00\rangle=|\varphi_{+1}^0\cdots\varphi_{+N}^0|. \tag{B.1}$$

The effective one-electron potential is chosen as

$$\tilde{V}=V+\sum_{i}^{N} W_i-\frac{1}{2}\sum_{i}^{N}|\varphi_i\rangle\sum_{j}^{N} W_{ij}\langle\varphi_i|=\sum_{i}^{N}\tilde{V}_i. \tag{B.2}$$

The W_i and W_{ij} are the electron interaction operators and integrals, respectively, including the exchange terms. For choice (B.2) of the effective potential $\tilde{V}$, the total energy is the sum of occupied orbital energies:

$$E^{00}=\sum_{i}^{N}\epsilon_i^{00}. \tag{B.00}$$

We introduce the approximate relativistic r-th order lower 2-component spinors

$$\varphi^{\text{or}}_{-i}=\boldsymbol{\sigma p}\varphi^{\text{or}}_{+i}/2c \tag{B.3}$$

and the "orthogonalized" functions χ

$$\chi=\left(1-\sum_{j}^{N}|\varphi^{00}_{+j}\rangle\langle\varphi^{00}_{+j}|\right)\varphi. \tag{B.4}$$

With these definitions, the perturbation energies can be expressed as

$$E^{0,1}=\sum_{i}^{N}\langle\varphi^{00}_{-i}|\tilde{V}^0-\epsilon_i^{00}|\varphi^{00}_{-i}\rangle \tag{B.01}$$

$$\begin{aligned}E^{0,2}=\sum_{i}^{N}\{&\langle\varphi^{00}_{-i}|(\tilde{V}^0-\epsilon_i^{00})^2|\varphi^{00}_{-i}\rangle\\&-\langle\varphi^{00}_{+i}|p^2|\varphi^{00}_{+i}\rangle\epsilon_i^{01}/2+\langle\varphi^{00}_{-i}|\tilde{V}^0-\epsilon_i^{00}|\boldsymbol{\sigma p}\chi^{01}_{+i}\rangle\}/2c^2\\&-\sum_{i\neq j}^{N}\langle\varphi^{00}_{-i}|\tilde{V}^0-(\epsilon_i^{00}+\epsilon_j^{00})/2|\varphi^{00}_{-j}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-i}\rangle\end{aligned} \tag{B.02}$$

$$E^{1,0}=\sum_{i}^{N}\langle\varphi^{00}_{+i}|\tilde{V}^1|\varphi^{00}_{+i}\rangle \tag{B.10}$$

$$E^{2,0}=\sum_{i}^{N}\{\langle\varphi^{00}_{+i}|\tilde{V}^1|\chi^{10}_{+i}\rangle+\langle\varphi^{00}_{+i}|\tilde{V}^2|\varphi^{00}_{+i}\rangle\}. \tag{B.20}$$

The higher-order terms are given by rather lengthy expressions:

$$\begin{aligned}E^{1,1}=&\sum_{i}^{N}\langle\varphi^{00}_{-i}|\tilde{V}^1-\epsilon_i^{10}|\varphi^{00}_{-i}\rangle+\operatorname{Re}\sum_{i\neq j}^{N}\langle\varphi^{00}_{+i}|\tilde{V}^1|\varphi^{00}_{+j}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-i}\rangle\\&+2\operatorname{Re}\sum_{i}^{N}\langle\varphi^{00}_{-i}|\tilde{V}^0-\epsilon_i^{00}|\chi^{10}_{-i}\rangle\\&\textbf{or}\\&+2\operatorname{Re}\sum_{i}^{N}\langle\varphi^{00}_{+i}|\tilde{V}^1|\chi^{01}_{+i}\rangle\end{aligned} \tag{B.11}$$

In the following, only one of the equivalent forms is given.

$$\begin{aligned}E^{1,2}=\sum_{i}^{N}\{&\langle\chi^{01}_{+i}|\tilde{V}^1-\epsilon_i^{10}|\chi^{01}_{+i}\rangle+2\operatorname{Re}\langle\chi^{01}_{-i}|\tilde{V}^1-\epsilon_i^{10}|\varphi^{00}_{-i}\rangle\\&+2\operatorname{Re}\langle\varphi^{00}_{-i}|(\tilde{V}^0-\epsilon_i^{00})(\tilde{V}^1-\epsilon_i^{10})|\varphi^{00}_{-i}\rangle/2c^2-\langle\varphi^{00}_{-i}|E^{1,1}|\varphi^{00}_{-i}\rangle\}\\&-\sum_{i\neq j}^{N}\{\langle\varphi^{00}_{+i}|\tilde{V}^1|\varphi^{00}_{+j}\rangle\cdot\langle\chi^{01}_{+j}|\chi^{01}_{+i}\rangle\\&+\langle\varphi^{00}_{-i}|\tilde{V}^1-\epsilon_i^{10}|\varphi^{00}_{-i}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-j}\rangle\\&-\langle\varphi^{00}_{-i}|\tilde{V}^1-\epsilon_i^{10}|\varphi^{00}_{-j}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-i}\rangle\}\end{aligned}$$

$$
\begin{aligned}
&+2\,\mathrm{Re}\sum_{i}^{N}\{\langle\varphi^{00}_{-i}|(\tilde{V}^{0}-\epsilon^{00}_{i})^{2}|\chi^{10}_{-j}\rangle/2c^{2}\\
&+\langle\chi^{01}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\chi^{10}_{-i}\rangle\\
&-\langle\chi^{01}_{+i}|\epsilon^{01}_{i}|\chi^{10}_{+i}\rangle-\langle\chi^{10}_{-i}|\epsilon^{01}_{i}|\varphi^{00}_{-i}\rangle\}\\
&+2\,\mathrm{Re}\sum_{i\neq j}^{N}\{\langle\varphi^{00}_{-i}|\tilde{V}^{0}-(\epsilon^{00}_{i}+\epsilon^{00}_{j})/2|\varphi^{00}_{-j}\rangle\langle\varphi^{00}_{+j}|\tilde{V}^{1}|\varphi^{00}_{+i}\rangle/2c^{2}\\
&-\langle\varphi^{00}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\varphi^{00}_{-j}\rangle\langle\chi^{10}_{-j}|\varphi^{00}_{-i}\rangle\\
&-\langle\varphi^{00}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\chi^{10}_{-j}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-i}\rangle\\
&+\langle\varphi^{00}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\chi^{10}_{-i}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-j}\rangle\\
&+\langle\varphi^{00}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{j}|\chi^{01}_{-j}\rangle\langle\varphi^{00}_{+i}|\tilde{V}^{1}|\varphi^{00}_{+j}\rangle/(\epsilon^{00}_{i}-\epsilon^{00}_{j})\}
\end{aligned}
\tag{B.12}
$$

$$
\begin{aligned}
E^{2,1}=&\sum_{i}^{N}\{\langle\varphi^{00}_{-i}|\tilde{V}^{2}-\epsilon^{20}_{i}|\varphi^{00}_{-i}\rangle+\langle\chi^{10}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\chi^{10}_{-i}\rangle-\langle\chi^{10}_{+i}|\epsilon^{01}_{i}|\chi^{10}_{+i}\rangle\}\\
&-\sum_{i\neq j}^{N}\{\langle\varphi^{00}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\varphi^{00}_{-j}\rangle\langle\chi^{10}_{+j}|\chi^{10}_{+j}\rangle+\langle\varphi^{00}_{+i}|\tilde{V}^{2}|\varphi^{00}_{+j}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-i}\rangle\\
&+\langle\varphi^{00}_{+i}|\tilde{V}^{1}|\chi^{10}_{+j}\rangle\langle\varphi^{00}_{-j}|\varphi^{00}_{-i}\rangle+\langle\varphi^{00}_{+i}|\tilde{V}^{1}|\varphi^{00}_{+j}\rangle\langle\chi^{10}_{+j}|\chi^{01}_{+i}\rangle\\
&-\left|\langle\varphi^{00}_{+i}|\tilde{V}^{1}|\varphi^{00}_{+j}\rangle\right|^{2}\cdot\epsilon^{01}_{i}/(\epsilon^{00}_{i}-\epsilon^{00}_{j})^{2}\}\\
&+2\,\mathrm{Re}\sum_{i}^{N}\{\langle\varphi^{00}_{+i}|\tilde{V}^{2}|\chi^{01}_{+i}\rangle+\langle\chi^{10}_{-i}|\tilde{V}^{1}-\epsilon^{10}_{i}|\varphi^{00}_{-i}\rangle\\
&+\langle\chi^{10}_{+i}|\tilde{V}^{1}-\epsilon^{01}_{i}|\varphi^{00}_{+i}\rangle\}\\
&-2\,\mathrm{Re}\sum_{i\neq j}^{N}\{\langle\varphi^{00}_{+i}|\tilde{V}^{1}|\varphi^{00}_{+j}\rangle\cdot\langle\chi^{10}_{-j}|\varphi^{00}_{-i}\rangle\}.
\end{aligned}
\tag{B.21}
$$

$$
E^{3,0}=\sum_{i}^{N}\{\langle\chi^{10}_{+i}|\tilde{V}^{1}-\epsilon^{10}_{i}|\chi^{10}_{+i}\rangle+2\,\mathrm{Re}\langle\varphi^{00}_{+i}|\tilde{V}^{2}|\chi^{10}_{+i}\rangle+\langle\varphi^{00}_{+i}|\tilde{V}^{3}|\varphi^{00}_{+i}\rangle\}
\tag{B.30}
$$

$$
\begin{aligned}
E^{0,3}=&\sum_{i}^{N}\{\langle\varphi^{00}_{-i}|(\tilde{V}^{0}-\epsilon^{00}_{i})^{3}|\varphi^{00}_{-i}\rangle-\epsilon^{02}_{i}\langle\varphi^{00}_{-i}|\varphi^{00}_{-i}\rangle-(\epsilon^{01}_{i})^{2}/c^{2}\\
&+2\,\mathrm{Re}\langle\varphi^{00}_{-i}|(\tilde{V}^{(0)}-\epsilon^{00}_{i})^{2}|\chi^{01}_{-i}\rangle/2c^{2}\\
&+\langle\chi^{10}_{-i}|\tilde{V}^{1}-\epsilon^{00}_{i}|\chi^{10}_{-i}\rangle-\epsilon^{01}_{i}\langle\chi^{01}_{+i}|\chi^{01}_{+i}\rangle\}\\
&+\sum_{i\neq j}^{N}\{|\langle\varphi^{00}_{-i}|\varphi^{00}_{-j}\rangle(\epsilon^{01}_{i}+\epsilon^{01}_{j})/2-|\langle\varphi^{00}_{-i}|\tilde{V}^{(0)}-\frac{\epsilon^{00}_{i}+\epsilon^{00}_{j}}{2}|\varphi^{00}_{-j}\rangle|^{2}/c^{2}\\
&-\langle\varphi^{00}_{-i}|\varphi^{00}_{-j}\rangle\langle\varphi^{00}_{-j}|\tilde{V}^{(0)2}-(\epsilon^{00}_{i}+\epsilon^{00}_{j})\tilde{V}^{(0)}+(\epsilon^{00^{2}}_{i}+\epsilon^{00}_{j})^{2}|\varphi^{00}_{-i}\rangle/2c^{2}\\
&-\langle\varphi^{00}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\varphi^{00}_{-j}\rangle\langle\varphi^{00}_{-j}|\tilde{V}^{0}-\epsilon^{00}_{i}|\varphi^{00}_{-i}\rangle\langle\varphi^{00}_{-i}|\varphi^{00}_{-i}\rangle/(\epsilon^{00}_{i}-\epsilon^{00}_{j})\\
&+2\,\mathrm{Re}\langle\varphi^{00}_{-i}|\tilde{V}^{0}-\epsilon^{00}_{i}|\varphi^{00}_{-j}\rangle\langle\varphi^{00}_{-j}|\tilde{V}^{0}-\epsilon^{00}_{i}|\chi^{01}_{-i}\rangle/(\epsilon^{00}_{i}-\epsilon^{00}_{j})|\}\\
&+\sum_{i\neq j\neq k}^{N}\langle\varphi^{00}_{-i}|\varphi^{00}_{-j}\rangle\langle\varphi^{00}_{-k}|\varphi^{00}_{-i}\rangle\langle\varphi^{00}_{-j}|\tilde{V}^{0}-(\epsilon^{00}_{i}+\epsilon^{00}_{j}+\epsilon^{00}_{k})/6|\varphi^{00}_{-k}\rangle
\end{aligned}
\tag{B.03}
$$

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