Relativistic Quantum Chemistry
—
The Fundamental Theory of Molecular Science

Markus Reiher and Alexander Wolf

List of Corrections
for First Edition

July 12, 2014

Preface

After publication of the first edition of our book *Relativistic Quantum Chemistry* in January 2009, we got aware of typos in equations, which appear to be unavoidable when writing a book from scratch. While the publisher is now in possession of an updated version for printing the second edition later this year, in which we also revised parts of the text, we would like to provide the readers of the first edition with a list of **corrections for misprinted equations**.

We are especially grateful to our students, co-workers, and colleagues who had drawn our attention to some of these issues: Katharina Boguslawski, Arndt Finkelmann, Sam Fux, Moritz Haag, Mickael Hubert, Christoph Jacob, Bogumil Jeziorski, Stefan Knecht, Tobias Krähenmann, Vincent Liegeois, Koni Marti, Edit Mátyus, Daoling Peng, Maren Podewitz, Trond Saue, Benjamin Simmen, and Thomas Weymuth.

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Corrections of Equations

- Eq. (3.147); central line of this equation: ′+′ under square root should read ′−′
- Eq. (3.205):

$$t'_{12} = \frac{|\boldsymbol{r}'_1(t'_1) - \boldsymbol{r}'_2(t'_2)|}{c} = \frac{|\boldsymbol{r}'_1(t'_1) - \boldsymbol{r}'_2(t'_1)|}{c}$$

- Last line of Eq. (3.239):

$$= \quad r_{12} + \frac{1}{2}\frac{(\boldsymbol{r}_{12}\cdot\dot{\boldsymbol{r}}_2)^2}{r_{12}c^2} - \frac{r_{12}}{2}\frac{\dot{\boldsymbol{r}}_2^2 - \boldsymbol{r}_{12}\cdot\ddot{\boldsymbol{r}}_2}{c^2} + O(c^{-3})$$

- Eq. (3.241): charge q_2 is missing on r.h.s.
- Eq. (4.54):

$$\langle\Psi_n|\hat{V}\Psi_m\rangle = \langle\hat{V}\Psi_m|\Psi_n\rangle^\star = \langle\Psi_m|\hat{V}\Psi_n\rangle^\star = \langle\hat{V}\Psi_n|\Psi_m\rangle$$

- Eq. (4.55):

$$\langle\Psi_n|\hat{\boldsymbol{p}}\Psi_m\rangle = \langle\Psi_n| - \mathrm{i}\hbar\nabla\Psi_m\rangle \overset{p.I.}{=} \langle -\mathrm{i}\hbar\nabla\Psi_n|\Psi_m\rangle = \langle\hat{\boldsymbol{p}}\Psi_n|\Psi_m\rangle$$

- Eq. (4.77): the factor $(\mathrm{i}/\hbar)$ is missing after the second equality sign.
- Eqs. (4.79), (4.80): $\hbar^2$ should be $\hbar$ (twice in both eqs.)
- Eq. (4.83): missing square on the r.h.s.
- Eq. (4.100): $1/r^2$ factor missing on l.h.s.
- Eq. (4.103):

$$\hat{T} = \frac{\hat{\boldsymbol{p}}^2}{2m} = \frac{1}{2m}\left[\frac{1}{r^2}\hat{\boldsymbol{l}}^2 - \hbar^2\left(\frac{1}{r}\frac{\partial}{\partial r}r\right)^2\right] = \frac{\hat{\boldsymbol{l}}^2}{2mr^2} + \frac{\hat{p}_r^2}{2m}$$

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- Eq. (4.130): missing global $\mp$ sign for $Y_{1(\pm 1)}$
- Eq. (5.51):

$$(\gamma^0)^2 = 1, \text{ while } (\gamma^i)^2 = -\mathbf{1}_4 \quad \text{and} \quad (\gamma^0)^\dagger = \gamma^0, \text{ while } (\gamma^i)^\dagger = -\gamma^i$$

- Eq. (5.52):

$$\{\gamma^\mu, \gamma^\nu\} \;=\; 2g^{\mu\nu}\mathbf{1}_4 \;=\; \begin{cases} 0 & \text{if } \mu \neq \nu \\ 2 & \text{if } \mu = \nu = 0 \\ -2 & \text{if } \mu = \nu \in \{1,2,3\} \end{cases} \tag{1.1}$$

- Eq. (5.88):

$$\hat{p}_i \exp\left[-\mathrm{i}\frac{p \cdot x}{\hbar}\right] = -\mathrm{i}\hbar\frac{\partial}{\partial x_i}\exp\left[-\mathrm{i}\frac{p \cdot x}{\hbar}\right] = p_i \exp\left[-\mathrm{i}\frac{p \cdot x}{\hbar}\right]$$

- Eq. (5.138): division by $\hbar$ on the r.h.s. missing
- Eq. (6.13):

$$\Psi^{nr}(\boldsymbol{r}) \quad \longrightarrow \quad \Psi^{nr}_{nlm}(\boldsymbol{r}) = R^{nr}_{nl}(r) Y_{lm}(\vartheta, \varphi) = \frac{P^{nr}_{nl}(r)}{r} Y_{lm}(\vartheta, \varphi)$$

- The definition of the operator $\boldsymbol{k}$ requires a global minus sign in order to match the convention that $s_{1/2}$ shells are assigned a negative κ quantum number as stated in Table 6.1. This convention then requires to exchange the right-hand sides in the two expressions for κ in Eqs. (6.37) and (6.38) and implies a global sign change in Eq. (6.36).
- Eq. (6.118): delete c in front of the square root in the denominator
- Text before Eq. (6.111) should read:
"Let us assume that this is the case for some n_r. Then, the recursion relations of Eqs. (6.92) and (6.93) read for $p_{n_r} = p_{i-1}$ and $q_{n_r} = q_{i-1}$ (with $p_i = q_i = 0, \forall\, i > n_r$),"
- Eq. (6.145):
The 3rd component of the ground-state spinor for $m_j = -1/2$ is lacking a minus sign in the exponential function depending on one of the angles, which should read $e^{-\mathrm{i}\varphi}$.
- Eq. (8.11):

$$\hat{\phi}_{i,\text{unret.}}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \frac{q_i}{r_{ij}} \quad \text{and} \quad \hat{\boldsymbol{A}}_{i,\text{unret.}}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \boldsymbol{\alpha}_i \frac{q_i}{r_{ij}} \quad , \quad i, j \in \{1, 2\}$$

- Eq. (8.23):

$$j_c^\mu(\boldsymbol{r},t) = \Big(\underbrace{c\, q_e \sum_{nm} a_n^\star a_m e^{(-\mathrm{i}\omega_{mn} t)} \psi_n^\dagger \psi_m}_{\rho_c = q_e \rho\,;\ Eq.\ (5.45)} \,,\ \underbrace{q_e c \sum_{nm} a_n^\star a_m e^{(-\mathrm{i}\omega_{mn} t)} \psi_n^\dagger \boldsymbol{\alpha} \psi_m}_{\boldsymbol{j}_c = q_e \boldsymbol{j}\,;\ Eq.\ (5.46)} \Big)$$

- Eq. (8.26): j_c^μ instead of j^μ
- Eqs. (8.27), (8.28), (8.29), (8.30), (8.32), (8.36): sum sign must be in front of expansion coefficients
- Eqs. (8.29) and (8.30):

$$\phi(\boldsymbol{r},t) = q_e \sum_{nm} a_n^\star a_m\, e^{(\mathrm{i}\omega_{nm} t)} \int \mathrm{d}^3 r' \psi_n^\dagger(\boldsymbol{r}') \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{\left(\mathrm{i}\omega_{mn} |\boldsymbol{r}-\boldsymbol{r}'|/c\right)} \psi_m(\boldsymbol{r}')$$

$$\boldsymbol{A}(\boldsymbol{r},t) = q_e \sum_{nm} a_n^\star a_m\, e^{(\mathrm{i}\omega_{nm} t)} \int \mathrm{d}^3 r' \psi_n^\dagger(\boldsymbol{r}') \frac{\boldsymbol{\alpha}}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{\left(\mathrm{i}\omega_{mn} |\boldsymbol{r}-\boldsymbol{r}'|/c\right)} \psi_m(\boldsymbol{r}')$$

- Eq. (8.31):

$$V_{ee} = \frac{1}{2c} \int \mathrm{d}^3 r_1\, j_c^\mu(1) A_\mu(1) = \frac{1}{2c^2} \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2\, \frac{j_c^\mu(1) j_{c,\mu}(2)}{r_{12}}$$

- Eqs. (8.33), (8.38), (8.39): Indices at ω must be exchanged
- Eq. (8.145):

$$\Gamma^A_{ijkl} = \sum_{IJ} C^\star_{IA} C_{JA} \sum_{KL} B^\star_{KI} B_{LJ} T^{KL}_{ikjl}$$

- Eq. (8.196): subscript on r.h.s. needs to be μ instead of ν
- Eq. (8.197): 2nd row lacks the $1/2m_e$ pre-factor
- In Eqs. (8.199)–(8.203) the three-dimensional δ-distribution, $\delta^{(3)}(\boldsymbol{s}-\boldsymbol{r})$, is meant and the $\boldsymbol{\alpha}$ vector operator must carry a particle index (inherited by the accompanying momentum operator) as the tensor notation is not used. Accordingly, Eqs. (8.204) and (8.205) should then read

$$\frac{\partial}{\partial t} \langle \hat{\rho}_{\boldsymbol{r}} \rangle = -\nabla \cdot \left\langle \Psi \middle| \underbrace{\sum_{i=1}^{N} c \boldsymbol{\alpha}_i \delta^{(3)}(\boldsymbol{r}_i - \boldsymbol{r})}_{\equiv \hat{\boldsymbol{j}}_{\boldsymbol{r}}} \middle| \Psi \right\rangle$$

$$\boldsymbol{j} \equiv \left\langle \Psi \middle| \hat{\boldsymbol{j}}_{\boldsymbol{r}} \middle| \Psi \right\rangle$$

- Eqs. (8.211) and (8.212): 3rd term on r.h.s must be divided by q_e as j^μ is the probability and not the charge 4-current

- Eq. (9.31):

$$\hat{H}_{el} = \sum_i^N \begin{pmatrix} m_e c^2 + V_{nuc}(r_i) & -\mathrm{i}c\left(\frac{\boldsymbol{\sigma}\cdot\boldsymbol{r}_i}{r_i}\right)\left[\frac{\hbar}{r_i}\frac{\partial}{\partial r_i}r_i - \frac{\boldsymbol{k}_i}{r_i}\right] \\ -\mathrm{i}c\left(\frac{\boldsymbol{\sigma}\cdot\boldsymbol{r}_i}{r_i}\right)\left[\frac{\hbar}{r_i}\frac{\partial}{\partial r_i}r_i - \frac{\boldsymbol{k}_i}{r_i}\right] & -m_e c^2 + V_{nuc}(r_i) \end{pmatrix}$$
$$+\sum_{j<i}^N \sum_{\nu=0}^{\infty} \frac{r^{\nu}_{<\in\{i,j\}}}{r^{\nu+1}_{>\in\{i,j\}}}\frac{4\pi}{2\nu+1}\sum_{m=-\nu}^{\nu} Y^\star_{\nu m}(\vartheta_i,\varphi_i)Y_{\nu m}(\vartheta_j,\varphi_j)$$

- Eqs. (9.91), (9.94), (9.97) : h_{ij} should be h^D_{ij}

- Eq. (10.7):

$$\psi_i^S = \frac{c}{2m_e c^2 - W + \epsilon_i}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})\psi_i^L \approx \frac{\boldsymbol{\sigma}\cdot\boldsymbol{\pi}}{2m_e c}\psi_i^L$$

- Eqs. (10.11) and (10.13): The prefactors of the STO and GTO small-component radial functions, respectively, need to be corrected:

$$Q_\mu^{\mathrm{STO}}(r_A) = N_\mu^S\left[(l_\mu+1) - \zeta_\mu r_A\right] r_A^{l_\mu}\exp\left(-\zeta_\mu r_A\right)$$
$$Q_\mu^{\mathrm{GTO}}(r_A) = N_\mu^S\left[(l_\mu+1) - 2\zeta_\mu r_A^2\right] r_A^{l_\mu}\exp\left(-\zeta_\mu r_A^2\right)$$

(note that we have omitted the κ_μ quantum number that results from a transformation of $(\boldsymbol{\sigma}\cdot\boldsymbol{p})$ to spherical coordinates for the sake of simplicity)

- Eqs. (10.15), (10.16) reduce to:

$$\mathrm{cGTO}_\mu(\boldsymbol{r}_A) = N_\mu^L\, x^{\alpha_\mu}y^{\beta_\mu}z^{\gamma_\mu}\exp\left(-\zeta_\mu^L r_A^2\right)$$

- Eq. (11.25):

$$f_- = \frac{1}{\sqrt{1+XX^\dagger}}\Big\{V - 2mc^2 - c\,\boldsymbol{\sigma}\cdot\boldsymbol{p}X^\dagger$$
$$-Xc\,\boldsymbol{\sigma}\cdot\boldsymbol{p} + XVX^\dagger\Big\}\frac{1}{\sqrt{1+XX^\dagger}}$$

- Eq. (11.30): β is missing as a pre-factor for the last term on the r.h.s.

- Eq. (11.32):

$$\tan\left[2\omega(p)\right] = \frac{cp}{m_e c^2} = \frac{p}{m_e c}$$

- Eq. (11.84):

$$\mathcal{E}_{[2]} \quad = \quad -\beta\,\frac{\boldsymbol{p}^4}{8m_e^3c^2} - \frac{\left[\boldsymbol{\alpha}\cdot\boldsymbol{p},\left[\boldsymbol{\alpha}\cdot\boldsymbol{p},V\right]\right]}{8m_e^2c^2}$$

- In Eqs. (11.91) and (12.1), the product of unitary matrices is better consistently written with exchanged limits as $U = \prod_{i=\infty}^{0} U_i$.
- Eq. (12.54): $\boldsymbol{p}^2$ under the square root on the right hand side is lacking a subscript i.
- Eq. (13.73): $\hbar$ must be removed twice
- Eq. (13.74): global sign must be '+', prefactor should be $1/8$ and not $1/4$
- Eq. (13.75): $\hbar^2$ must be removed, no δ-distribution after the $1/r_{12}^3$ term
- Eq. (13.77):

$$\boldsymbol{p}_i\cdot\boldsymbol{E}_i = \mathrm{i}\hbar\frac{\Delta_i}{q_e}\left[V_{nuc}(i)+V_{ee}\right] = -\mathrm{i}\hbar\,4\pi\sum_{I=1}^{M} Z_I e\,\delta^{(3)}(\boldsymbol{r}_{iI}) + \mathrm{i}\hbar\,4\pi\sum_{j=1}^{N} e\delta^{(3)}(\boldsymbol{r}_{ij})$$

- Eq. (13.93): $c(\boldsymbol{\sigma}\cdot\boldsymbol{p})^2$ should read $(c\boldsymbol{\sigma}\cdot\boldsymbol{p})^2$
- Eq. (15.41):

$$H_6 = \frac{e}{m_e c}\sum_i \boldsymbol{B}_i\cdot\boldsymbol{s}_i + \frac{e}{m_e c}\sum_i \boldsymbol{p}_i\cdot\boldsymbol{A}_i + \frac{e^2}{2m_e c^2}\sum_i \boldsymbol{A}_i^2$$

- In Eqs. (15.82) and (15.83), $\boldsymbol{\alpha}$ must carry the subscript '1' and the three-dimensional δ-distribution, $\delta^{(3)}(\boldsymbol{s}-\boldsymbol{r})$, is meant. Note also that the unitary transformation to be considered is the many-electron unitary transformation U^{tot} defined in chapter 12.
- Eq. (15.99):

$$X_{ij}^{(I),nuc}(\boldsymbol{R}_I) = \sum_{\substack{J=1\\ J\neq I}}^{M} Z_J e\frac{3(\boldsymbol{R}_J-\boldsymbol{R}_I)_i(\boldsymbol{R}_J-\boldsymbol{R}_I)_j - |\boldsymbol{R}_J-\boldsymbol{R}_I|^2\delta_{ij}}{|\boldsymbol{R}_J-\boldsymbol{R}_I|^5}$$

- Eq. (16.8): The c^2 in the denominator in the middle must be deleted and the E on the right hand side lacks a 'nr' superscript.
- Eq. (D.20):

$$\begin{aligned}\boldsymbol{\pi}\times\boldsymbol{\pi} &= -\frac{q_e}{c}\left(\boldsymbol{p}\times\boldsymbol{A} + \boldsymbol{A}\times\boldsymbol{p}\right)\\ &= \mathrm{i}\hbar\frac{q_e}{c}\left(\nabla\times\boldsymbol{A} + \boldsymbol{A}\times\nabla\right)\end{aligned}$$