Relativistic Quantum Chemistry
—
The Fundamental Theory of Molecular Science

Markus Reiher and Alexander Wolf

List of Corrections
for First Edition

November 27, 2010

Preface

After publication of the first edition of our book *Relativistic Quantum Chemistry* in January 2009, we got aware of some typos in equations which are apparently unavoidable when writing a book from scratch. While the publisher is now in possession of an updated version of the first edition for reprinting, in which we also fixed some minor typos in the text, we would like to provide a list of **corrections for missprinted equations** to the readers of the first edition.

We are especially grateful to our students and co-workers Katharina Boguslawski, Arndt Finkelmann, Sam Fux, Moritz Haag, Dr. Christoph Jacob, Dr. Vincent Liegeois, Koni Marti, Dr. Edit Mátyus, Maren Podewitz, and Thomas Weymuth who were engaged in exercise classes to lectures held on the subject at ETH Zurich and who drew our attention to several of these typos.

Markus Reiher and Alexander Wolf *Zürich, November 2010*

Corrections for *Relativistic Quantum Chemistry.* Markus Reiher and Alexander Wolf
ISBN: 978-3-527-31292-4

1
Corrections of Equations

- 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):

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

- 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. (4.100): $1/r^2$ factor missing on l.h.s.
- Eq. (4.103):

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

- Eq. (5.88):

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

Corrections for *Relativistic Quantum Chemistry.* Markus Reiher and Alexander Wolf
ISBN: 978-3-527-31292-4

- Eq. (6.13):

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

- 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. (8.11):

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

- Eq. (8.23):

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

- Eq. (8.26): j^{μ}_{c} 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):

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

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

- Eq. (8.31):

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

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

- Eq. (8.145):

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

- 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

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

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

- Eq. (9.31):

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

- 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. (10.15), (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):

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

- 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):

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

- 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. (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. (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. (D.20):

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