Quantum electrodynamics corrections to the $2P$ fine splitting in Li

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Abstract

We consider quantum electrodynamics (QED) corrections to the fine splitting $E(2P_{3/2}) - E(2P_{1/2})$ in the Li atom. We derive complete formulas for the $m\alpha^6$ and $m\alpha^7\ln\alpha$ contributions and calculate them numerically using highly optimized, explicitly correlated basis functions. The obtained results resolve disagreement between measurements and lay the foundations for investigation of QED effects in light, many-electron atoms.

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INTRODUCTION

The inclusion of relativistic effects and correlations between electrons in atomic systems gives rise to some fundamental problems related to the many-electron Dirac equation. This equation has to include two and more electron-positron pairs to be in accordance with Quantum Electrodynamics (QED). Moreover, achieving the correct nonrelativistic limit for the energy difference between states of the same orbital momentum is highly problematic [1]. For this reason, no accurate relativistic calculation of the lithium $2P_{3/2} - 2P_{1/2}$ splitting has been performed so far. For light atomic systems the best approach relies on nonrelativistic QED theory, where relativistic and QED effects are treated perturbatively, while the nonrelativistic Hamiltonian is solved using explicitly correlated basis sets. This approach has been successfully applied to helium [2, 3], lithium [4, 5], and beryllium atoms [6]. The helium fine structure is a very good example; it was calculated to the $m \alpha^7$ order and currently serves as one of the most precise QED tests in few-electron systems [7]. Conversely, theoretical results for lithium fine structure are much less accurate, and the various experiments are not always in agreement with each other and with the theory [10]. For example, long standing discrepancies in the isotope shift of the fine structure have been resolved only recently, and it would appear that the results from previous experiments and theoretical predictions were both incorrect [10, 11]. In this work we aim to significantly improve theoretical prediction of the lithium fine structure $2P_{3/2} - 2P_{1/2}$ by the complete calculation of the $m \alpha^6$ and $m \alpha^7 \ln \alpha$ contributions. We derive closed formulas for QED corrections and perform numerical calculations using explicitly correlated basis sets with Hylleraas and Gaussian functions. Such calculations have been performed by Douglas and Kroll for the helium fine structure of $^3P_J$ levels in Ref. [13]. It took 40 years to extend their two-electron $m \alpha^6$ result to an atom with three electrons, indicating that accurate calculations of QED effects in many electron systems is a challenging task.

LITHIUM FINE STRUCTURE

The leading $m \alpha^4$ order contribution $E_{fs}^{(4)}$, including the all-order electron g-factor, is obtained from the fine-structure Hamiltonian [12]

\[ E_{fs}^{(4)} = \langle \phi | H_{fs}^{(4)} | \phi \rangle \]  (1)
where

\[
H^{(4)}_{fs} = \sum_a \frac{Z \alpha}{4 r_a^3} \vec{\sigma}_a \left[ (g - 1) \vec{r}_a \times \vec{p}_a \right] 
+ \sum_{a \neq b} \frac{\alpha}{4 r_{ab}^3} \vec{\sigma}_a \left[ g \vec{r}_{ab} \times \vec{p}_b - (g - 1) \vec{r}_{ab} \times \vec{p}_a \right]
\] (2)

and \(g\) is the electron \(g\)-factor, and we employ natural units \(\hbar = c = \hbar = 1\). The wave function \(\phi\) in Eq. (1) is a solution of the nonrelativistic stationary Schrödinger equation corresponding to the \(2^2P\) state

\[
(H - E)\phi = 0
\] (3)

where

\[
H = \sum_a \frac{\vec{p}_a^2}{2} + V
\]

\[
V = \sum_a -\frac{Z \alpha}{r_a} + \sum_{b < a} \frac{\alpha}{r_{ab}}
\] (4)

The higher-order relativistic correction \(E^{(6)}\) is the subject of the present work. It can be expressed as the sum of the first- and second-order terms

\[
E^{(6)} = \langle \phi | H^{(4)} | \frac{1}{(E - H)^{\frac{1}{2}}} H^{(4)} | \phi \rangle + \langle \phi | H^{(6)}_{fs} | \phi \rangle,
\] (5)

where \[12\]

\[
H^{(4)} = H^{(4)}_A + H^{(4)}_B + H^{(4)}_C
\] (6)

\[
H^{(4)}_A = \sum_a \left\{ -\frac{\vec{p}_a^4}{8} + \frac{\pi Z}{2} \delta^3 (r_a) \right\}
\]

\[
+ \sum_{b < a} \left\{ \pi \delta^3 (r_{ab}) - \frac{1}{2} p_{i b} \left( \frac{\delta_{ij} - \delta_{ij}}{r_{ab}^2} \right) p_{j b} \right\}
\] (7)

\[
H^{(4)}_B = \sum_a \frac{Z}{4 r_a^3} \vec{\sigma}_a \cdot \vec{r}_a \times \vec{p}_a
\]

\[
+ \sum_{a \neq b} \frac{1}{4 r_{ab}^3} \vec{\sigma}_a \left( 2 \vec{r}_{ab} \times \vec{p}_b - \vec{r}_{ab} \times \vec{p}_a \right)
\] (8)

\[
H^{(4)}_C = \sum_{b < a} \frac{\sigma_{i a}^{ij} \sigma_{i j}^{ab}}{4 r_{ab}^3} \left( \delta_{ij} - 3 \frac{r_{ab}^i r_{ab}^j}{r_{ab}^2} \right)
\] (9)

3
and where $H^{(6)}_\text{fs}$ is an effective Hamiltonian of order $m\alpha^6$. $H^{(4)}_B$ above coincides with $H^{(4)}_\text{fs}$ in Eq. (2) for $g = 2$. The first derivation of $H^{(6)}_\text{fs}$ was performed for helium fine structure by Douglas and Kroll in [13] using the Salpeter-like approach. Numerical evaluation of this splitting has been performed to a high degree of precision in [14] and [15]. In this work we obtain $H^{(6)}_\text{fs}$ for lithium fine structure using a different approach, where nonrelativistic expansion is performed in the beginning at the Lagrangian level, see Ref. [16] and below.

In order to further improve theoretical predictions, the higher-order $m\alpha^7$ contribution is not neglected but instead is approximated by the numerically dominating logarithmic part. This part is obtained from the analogous result for helium fine structure [15, 17] by dropping the $\sigma^i \sigma^j$ terms because they do not contribute for states with total electron spin $S = 1/2$.

$$E^{(7)}_{\text{fs, log}} = \langle H^{(7)}_{\text{fs, log}} \rangle + 2 \langle H^{(4)}_B \frac{1}{(E_0 - H_0)'} H^{(5)}_{\text{log}} \rangle$$

$$H^{(5)}_{\text{log}} = \alpha^2 \ln[(Z\alpha)^{-2}] \left[ \frac{4Z}{3} \sum_a \delta^3(r_a) - \frac{7}{3} \sum_{b<a} \delta^3(r_{ab}) \right]$$

$$H^{(7)}_{\text{fs, log}} = \alpha^2 \ln[(Z\alpha)^{-2}] \left[ \frac{Z}{3} \sum_a i \vec{p}_a \times \delta^3(r_a) \vec{p}_a \cdot \vec{\sigma}_a ight. \left. - \frac{3}{4} \sum_{b\neq a} i \vec{p}_a \times \delta^3(r_{ab}) \vec{p}_a \cdot \vec{\sigma}_a \right].$$

The neglected higher-order corrections are the nonlogarithmic $m\alpha^7$ term and the finite nuclear mass corrections to the $m\alpha^6$ contribution. Corresponding uncertainties are 40 kHz and 15 kHz, what together with numerical uncertainties leads to about 6 ppm accuracy in the Li fine structure.

**SPIN-ORBIT HAMILTONIAN OF ORDER $m\alpha^6$**

Various approaches are possible to derive $m\alpha^6$ correction, and here we use a variant of nonrelativistic QED, where the effective NRQED Lagrangian is obtained by the Foldy-Wouthuysen (FW) transformation of a Dirac equation.

$$H_D = \vec{\alpha}(\vec{p} - e \vec{A}) + e A^0$$

$$H_{FW} = e^{iS} (H_D - i \partial_t) e^{-iS}$$

$$= H_D + i [S, H_D] - \frac{\partial S}{\partial t} + \ldots$$
We follow here Ref. [16] and additionally introduce further transformations to simplify the derivation of \(m\alpha^6\) operators. The \(H_{FW}\) obtained is

\[
H_{FW} = eA^0 + \frac{1}{2} \left( \pi^2 - e\bar{\sigma} \cdot \vec{B} \right) - \frac{1}{8} \left( \pi^4 - e\bar{\sigma} \cdot \vec{B} \pi^2 - \pi^2 e\bar{\sigma} \cdot \vec{B} \right) \\
- \frac{1}{8} \left( e\tilde{\nabla} \cdot \vec{E}_\parallel + e\bar{\sigma} \cdot \left( \vec{E}_\parallel \times \vec{p} - \vec{p} \times \vec{E}_\parallel \right) \right) + \frac{e^2}{2} \left(\bar{\sigma} \cdot \vec{E}_\parallel \times \vec{A} \right) \\
+ \frac{i e}{16} \left[ \bar{\sigma}(\vec{A} \times \vec{p} - \vec{p} \times \vec{A}) , \vec{p}^2 \right] + \frac{e^2}{8} \vec{E}_\parallel^2 + \frac{3}{32} \left\{ \vec{p}^2 , \vec{E}_\parallel \times \vec{p} \cdot \bar{\sigma} \right\} \\
+ \frac{5}{128} \left[ \vec{p}^2 , [\vec{p}^2 , e\alpha^0] \right] - \frac{3}{64} \left\{ \vec{p}^2 , \bigtriangledown^2(e\alpha^0) \right\} + \frac{\vec{p}^6}{16} \\
\tag{14}
\]

where \(\vec{E}_\parallel = -\tilde{\nabla} \alpha^0\). \(H_{FW}\) can be used to derive \(H^{(4)}\) as well as \(H^{(6)}\). Details of such derivation are presented in Ref. [16]. Here we re-derive \(H^{(6)}_{fs}\) with the use of a simpler, but equivalent, form of \(H_{FW}\) in Eq. (14). Let \(\vec{E}_a\) denote the static electric field at the position of particle \(a\)

\[
e \vec{E}_a \equiv -\bigtriangledown_a V = -Z \alpha \vec{r}_a / r_a^3 + \sum_{b \neq a} \alpha \vec{r}_{ab} / r_{ab}^3 \\
\tag{15}
\]

The vector potential at the position of particle \(a\), which is produced by all other particles, is

\[
e \vec{A}_a \equiv \sum_{b \neq a} \frac{\alpha}{2 r_{ab}} \left( \delta^{ij} + \frac{r_{ab} r_{ab}}{r_{ab}^3} \right) \vec{p}_b^j + \frac{\alpha}{2} \left( \bar{\sigma}_a \times \vec{r}_{ab} \right)^i \\
\tag{16}
\]

Following the derivation in Ref. [16], the higher-order contributions are

\[
H^{(6)}_{fs} = \sum_a \left\{ \frac{3}{16} p_a^2 e \vec{E}_a \times \vec{p}_a \cdot \bar{\sigma}_a + \frac{e}{4} \left( 2 p_a^2 \bar{\sigma}_a \cdot \vec{A}_a + p_a^4 \bar{\sigma}_a \cdot \bigtriangledown_a \times \vec{A}_a \right) + \frac{e^2}{2} \bar{\sigma}_a \cdot \vec{E}_a \times \vec{A}_a \right. \\
+ \frac{i e}{16} \left[ \bar{\sigma}_a \times \vec{p}_a \cdot \bar{\sigma}_a - \bar{\sigma}_a \cdot \vec{p}_a \times \vec{A}_a , p_a^2 \right] + \frac{e^2}{2} \vec{A}_a^2 \left\} + \sum_{b \neq a} \left\{ -\frac{i \pi \alpha}{8} \bar{\sigma}_a \cdot \vec{p}_a \times \delta^3(r_{ab}) \vec{p}_a \\
+ \frac{\alpha}{4} \left[ -\bar{\sigma}_a \times \vec{r}_{ab}, \frac{p_a^2}{2} \right] e \vec{E}_b + \left[ \frac{p_b^2}{2} , \left[ \bar{\sigma}_a \times \vec{r}_{ab}, \frac{p_a^2}{2} \right] \right] \vec{p}_b \right\} \\
\tag{17}
\]

Most of the terms in \(H^{(6)}_{fs}\) are obtained in the nonretardation approximation, which corresponds to replacing the electromagnetic fields in \(H_{FW}\) for the particle \(a\) with fields that come from all other particles, called \(b\). The last two are exceptions. The first term under the sum over \(a\) and \(b\) comes from a Coulomb interaction between electrons, where both electron vertices, instead of \(e A^0\), are of the form \(-\frac{1}{8m_e} \left[ e\tilde{\nabla} \cdot \vec{E}_\parallel + e\bar{\sigma} \cdot \left( \vec{E}_\parallel \times \vec{p} - \vec{p} \times \vec{E}_\parallel \right) \right]\), and the second term comes from the single transverse photon exchange with the electron vertices of the form \(-e \vec{p} \vec{A} / m\). The second-order
TABLE I: $m\alpha^6$ and $m\alpha^7$ ln $\alpha$ contributions to Li 2P fine splitting, in units $m\alpha^6$ and $m\alpha^7$ correspondingly

| Term                                                                 | Value          |
|----------------------------------------------------------------------|----------------|
| $\langle \phi | H_{fs}^{(6)} | \phi \rangle$                          | $-0.2021(16)$ |
| $\langle \phi | H_{B}^{(4)} \frac{12s}{E-H} H_{B}^{(4)} | \phi \rangle$ | $0.29349$     |
| $\langle \phi | H_{B}^{(4)} \frac{14s}{E-H} H_{B}^{(4)} | \phi \rangle$ | $-0.29594(2)$ |
| $2 \langle \phi | H_{B}^{(4)} \frac{12p}{(E-H)^2} H_{A}^{(4)} | \phi \rangle$ | $0.1953(17)$  |
| $\langle \phi | H_{B}^{(4)} \frac{12p}{(E-H)^2} H_{B}^{(4)} | \phi \rangle$ | $0.5397(5)$   |
| $\langle \phi | H_{B}^{(4)} \frac{14p}{(E-H)} H_{B}^{(4)} | \phi \rangle$ | $-0.4506(2)$  |
| $\langle \phi | H_{C}^{(4)} \frac{14p}{(E-H)} H_{C}^{(4)} | \phi \rangle$ | $0.00623$     |
| $2 \langle \phi | H_{B}^{(4)} \frac{14p}{(E-H)} H_{C}^{(4)} | \phi \rangle$ | $0.02090$     |
| $\langle \phi | H_{B}^{(4)} \frac{12d}{(E-H)} H_{B}^{(4)} | \phi \rangle$ | $-0.75113(2)$ |
| $\langle \phi | H_{B}^{(4)} \frac{14d}{(E-H)} H_{B}^{(4)} | \phi \rangle$ | $0.73327(2)$  |
| $\langle \phi | H_{C}^{(4)} \frac{14d}{(E-H)} H_{C}^{(4)} | \phi \rangle$ | $0.00008$     |
| $2 \langle \phi | H_{B}^{(4)} \frac{14d}{(E-H)} H_{C}^{(4)} | \phi \rangle$ | $-0.00001$    |
| $\langle \phi | H_{C}^{(4)} \frac{14p}{(E-H)} H_{C}^{(4)} | \phi \rangle$ | $-0.00213$    |
| $E_{fs}^{(6)}$ | $0.0871(24)$ |
| $\langle \phi | H_{fs,log}^{(7)} | \phi \rangle$                          | $-0.73638$    |
| $2 \langle \phi | H_{B}^{(4)} \frac{12p}{(E-H)^2} H_{log}^{(5)} | \phi \rangle$ | $1.7839(4)$   |
| $E_{fs,log}^{(7)}$ | $1.0475(4)$ |

contribution in Eq. (5) is split into parts coming from intermediate states of the specified angular momentum and the spin. These parts are defined in Table I. Most of them can be calculated as they stand. Only the matrix elements involving $H_{A}^{(4)}$ and $\delta^3(r_a)$ need special treatment due to the high singularity of these operators.
SPIN REDUCTION OF MATRIX ELEMENTS

The wave function of the $^2P$ state in the three-electron system is represented as

$$\Phi^i = \frac{1}{\sqrt{6}} A [\phi^i(r_1, r_2, r_3) [\alpha(1) \beta(2) - \beta(1) \alpha(2)] \alpha(3)]$$ \hspace{0.5cm} (18)

where $A$ denotes antisymmetrization and $\phi^i(r_1, r_2, r_3)$ is a spatial function with Cartesian index $i$ that comes from any of the electrons coordinate, $\phi^i = r^i_a \phi$. The normalization we assume is

$$1 = \sum_i \langle \Phi^i' | \Phi^i \rangle = \sum_i \langle \phi^i(r_1, r_2, r_3) | P[c_{123} \phi^i(r_1, r_2, r_3)] \rangle$$ \hspace{0.5cm} (19)

where $P$ denotes a sum of all permutations of $1,2,3$ subscripts. The $^2P_{1/2}$ and $^2P_{3/2}$ wave functions are constructed using Clebsch-Gordon coefficients. Expectation values with these wave functions can be reduced to spatial expectation values with algebraic prefactor for $J = 1/2, 3/2$, accordingly; i.e. the first-order matrix elements take the form

$$\langle \Phi^i' | O | \Phi \rangle = \{1, 1\} \langle \phi'^i(r_1, r_2, r_3) | Q \ P[c_{123} \phi^i(r_1, r_2, r_3)] \rangle$$ \hspace{0.5cm} (20)

$$\langle \Phi^i' | \sum_a \vec{\sigma}_a \cdot \vec{Q}_a | \Phi \rangle = \{1, -1/2\} i \epsilon^{ijk} \langle \phi'^i(r_1, r_2, r_3) | \sum_a Q^j_a \ P[c_{123} \phi^j(r_1, r_2, r_3)] \rangle$$ \hspace{0.5cm} (21)

$$\langle \Phi^i' | \sum_{a \neq b} \vec{\sigma}_a \times \vec{\sigma}_b \cdot \vec{Q}_{ab} | \Phi \rangle = \{1, -1/2\} (-2 \epsilon^{ijk}) \langle \phi'^i(r_1, r_2, r_3) | \sum_{ab=12, 23, 31} (Q^j_{ab} - Q^j_{ba}) \ P[c_{123} \phi^k(r_1, r_2, r_3)] \rangle$$ \hspace{0.5cm} (22)

The second-order matrix elements can also been reduced to the spatial ones, with different prefactors similarly to those above.

NUMERICAL CALCULATIONS

The spatial function is represented as a linear combination of the Hylleraas \[18\]

$$\phi = e^{-\alpha_1 r_1 - \alpha_2 r_2 - \alpha_3 r_3} r_1^{n_1} r_2^{n_2} r_3^{n_3}$$ \hspace{0.5cm} (23)

or of the Gaussian functions \[19\]

$$\phi = e^{-\alpha_1 r_1^2 - \alpha_2 r_2^2 - \alpha_3 r_3^2}$$ \hspace{0.5cm} (24)
TABLE II: Symmetrization coefficients in spatial matrix elements

| (k, l, m) | $c_{klm}$ | $c_{F1}^{klm}$ | $c_{F2}^{klm}$ | $c_{F3}^{klm}$ |
|----------|-----------|----------------|----------------|----------------|
| (1, 2, 3) | 2         | 0              | 0              | 2              |
| (1, 3, 2) | -1        | 1              | -1             | -1             |
| (2, 1, 3) | 2         | 0              | 0              | 2              |
| (2, 3, 1) | -1        | -1             | 1              | -1             |
| (3, 1, 2) | -1        | 1              | -1             | -1             |
| (3, 2, 1) | -1        | -1             | 1              | -1             |

In the Hylleraas basis we use 6 sectors with different values of nonlinear parameters $w_i$ and a maximum value of $\Omega = n_1 + n_2 + n_3 + n_4 + n_5 = 13$, details are in [8, 9]. In Gaussian basis we use $N = 256, 512, 1024$, and 2048 functions with well-optimized nonlinear parameters for each basis function, separately. The accuracy achieved for nonrelativistic energies is about $10^{-13}$ in Hylleraas and $10^{-11}$ in Gaussian bases. The first-order matrix elements involving the Dirac $\delta$-function are calculated with Hylleraas basis; all other operators are calculated using Gaussians. Numerical results for the extrapolated value of $\langle H_{ls}^{(6)} \rangle$ are presented in Table III and the achieved precision is about $10^{-3}$. The evaluation of second-order matrix elements is much more demanding. They are obtained using the Gaussian basis, as follows. The resolvent $1/(E - H)$ for each angular momentum is represented in terms of functions with the appropriate Cartesian prefactor. Nonlinear parameters for intermediate states are optimized for each symmetric matrix element. For the asymmetric matrix elements, the basis is combined from two corresponding symmetric ones. The most computationally demanding matrix elements were these, which involve $H_A^{(4)}$ and $H_{\log}^{(5)}$ operators, and they are transformed to the regular form by the following transformations

$$H_A^{(4)} = [H_A^{(4)}]_r + \left\{ \sum_a \frac{Z}{4 r_a} - \sum_{b < a} \frac{1}{2 r_{ab}}, E - H \right\},$$

$$4\pi \delta^3(r_a) = 4\pi [\delta^3(r_a)]_r - \left\{ \frac{2}{r_a}, E - H \right\}.$$  

The resulting second order matrix elements became less singular and can readily be evaluated numerically. Numerical results for matrix elements are summarized in Table III. The achieved precision is of order $10^{-3}$ and better; similarly to the first-order matrix elements. Moreover, we
observed significant cancellations between $S = 1/2$ and $S = 3/2$ intermediate states, and between the first- and second-order terms. The final numerical result for the $m \alpha^6$ contribution in Table II is quite small but larger than the hydrogenic value $5/256 = 0.019531$, as it should be. Regarding the $m \alpha^7$ contribution, the second-order term is numerically dominant, and the contribution from $H_{fs, log}^{(7)}$ is more than twice smaller. Altogether, this correction is only 10 times smaller than the $m \alpha^6$ contribution and is significant in comparison to the accuracy of experimental values.

**SUMMARY**

We have performed accurate calculations of the fine structure in Li using the nonrelativistic QED approach. Relativistic and QED corrections are represented in terms of effective operators and are calculated using a highly accurate nonrelativistic wave function. Numerical results are summarized in Table III. The obtained theoretical results for the $^{6,7}$Li fine structure are in agreement with the recent experimental values of Ref. [10] and also with Refs. [20, 21], but are in disagreement with all the other ones. This demonstrates the capability of NRQED theory and the numerical approach based on explicitly correlated functions in achieving high-precision predictions for energies and energy splittings in light, few-electron atoms.

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TABLE III: Fine splitting of 2P-states in Li isotopes in MHz. $\delta E_{\text{fs}}$ is the hyperfine mixing correction. The uncertainty of $E_{\text{fs}}$(theo) comes mainly from numerical inaccuracies of $E_{\text{fs}}^{(6,0)}$ and from the neglect $E_{\text{fs,no log}}^{(7,0)}$, which is estimated by 25% of $E_{\text{fs, log}}^{(7,0)}$.

|                | $^6\text{Li}$                | $^7\text{Li}$                | Ref.    |
|----------------|-------------------------------|-------------------------------|---------|
| $E_{\text{fs}}^{(4,0)}$ | 10 053.707 2(83)              | 10 053.707 2(83)              | [8, 9]  |
| $E_{\text{fs}}^{(4,1)}$ | $-2.786 8(6)$                | $-2.389 1(5)$                | [8, 9]  |
| $E_{\text{fs}}^{(6,0)}$ | 1.63(5)                      | 1.63(5)                      |         |
| $E_{\text{fs}}^{(7,0)}$ | 0.15                          | 0.15                          |         |
| $\delta E_{\text{fs}}$ | 0.012 17                     | 0.159 16                     | [9]     |
| $E_{\text{fs}}$(theo)  | 10 052.72(6)                  | 10 053.25(6)                  |         |
| $E_{\text{fs}}$(exp)   | 10 052.779(17)                | 10 053.310(17)                | Brown   |
|                       | 10 052.76(22)                 | 10 053.24(22)                 | Brog    |
|                       |                                | 10 053.184(58)                | Orth    |
|                       | 10 052.964(50)                | 10 053.119(58)                | Noble   |
|                       | 10 052.044(91)                | 10 052.37(11)                 | Walls   |
|                       | 10 052.862(41)                | 10 051.999(41)                | Das     |

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