Relativistic many-body calculations of electric-dipole matrix elements, lifetimes and polarizabilities in rubidium.

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Electric-dipole matrix elements for ns – n′p, nd – n′p, and 6d – 4f transitions in Rb are calculated using a relativistic all-order method. A third-order calculation is also carried out for these matrix elements to evaluate the importance of the high-order many-body perturbation theory contributions. The all-order matrix elements are used to evaluate lifetimes of ns and np levels with n = 6, 7, 8 and nd levels with n = 4, 5, 6 for comparison with experiment and to provide benchmark values for these lifetimes. The dynamic polarizabilities are calculated for ns states of rubidium. The resulting lifetime and polarizability values are compared with available theory and experiment.

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I. INTRODUCTION

A recent proposal [1] for quantum computation utilizes the ground hyperfine states of a neutral atom as qubits, and realizes two-qubit quantum gates by conditional excitations to Rydberg states. The atoms are confined to the sites of an optical lattice, and the optical potential seen by the atom depends on the dynamic polarizability of the atom. Therefore, the atom will generally move in a different lattice potential when it is excited to the Rydberg state during the gate operation, which may cause motional heating and lead to decoherence. In a recent paper [2], we proposed two solutions to this problem by matching the ac polarizabilities of the atom in the ground and Rydberg states. In the first scheme, the polarizabilities are matched for the specific values of the lattice photon frequency between the resonances. In the second scheme, some accidental matches between transition energies are used to match the ground state polarizability with the polarizability of the selected Rydberg states (1p and 1p in the case of Rb). The elimination of motional decoherence is important in helping to design a high-fidelity two-qubit gate capable of meeting the error threshold for scalable quantum computation.

Despite the existence of high-precision measurements of the primary transition electric-dipole matrix elements in alkali-metal atoms, accurate experimental data for other transitions are lacking with the exception of a very few transitions in Cs owing to the study of parity nonconservation. In light of the importance of the atomic calculations for the quantum logic gate scheme with conditional excitations to Rydberg levels, we have calculated the electric-dipole matrix elements for subsequent evaluation of lifetimes and polarizabilities for a number of Rb levels. We note that the interest in this particular logic gate scheme with neutral atoms results from its potential for fast (sub-microsecond) gate operations.

We have performed all-order calculations of the 7s – np, 8s – np, 4d – np, 5d – np, and 6d – np electric-dipole matrix elements with n = 5, 6, 7 and 8, and of the 6d – 4f matrix elements. These results are combined with previous all-order calculations of the 5s – np and 6s – np matrix elements [3] to obtain values of the lifetimes of the 6s, 7s, 8s, 6p, 7p, 8p, 4d, 5d, and 6d levels. The lifetime of the 6d3/2 level is of special interest owing to the large discrepancies between existing experiments [1, 5]. The third-order matrix-element calculation has also been carried out to evaluate the importance of the higher-order contributions. The dynamic polarizabilities of the Rb ns states are also calculated for both low-lying and Rydberg levels. The evaluation of the accuracy of the polarizability calculations is conducted including a comparison between our data and other theory and experiment.

II. ELECTRIC-DIPOLE MATRIX ELEMENTS

The electric-dipole matrix elements for the 5s – 5p transitions were measured to high accuracy in [6] and matrix elements for ns – n′p transitions with n = 5, 6 and n′ = 5, 6, 7, 8 were calculated using a single-double (SD) all-order method in Refs. [3, 5]. In the present work, we have calculated matrix elements for 7s – np, 8s – np, 4d – np, 5d – np, and 6d – np transitions with n = 5, 6, 7 and 8 as well as 4f – 6d transitions using SD all-order method [6]. Very briefly, the wave function is represented as an expansion

$$|\Psi_v\rangle = \left[ 1 + \sum_{ma} \rho_{ma} a^\dagger_m a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a^\dagger_m a_1 a^\dagger_n a_2 a_a + \sum_{m \neq v} \rho_{mva} a^\dagger_m a_v + \sum_{mnva} \rho_{mnva} a^\dagger_m a_1 a^\dagger_n a_2 a_v \right] |\Phi_v\rangle,$$

(1)

where $\Phi_v$ is the lowest-order atomic state function, which is taken to be the frozen-core Dirac-Hartree-Fock (DHF) wave function of a state v; $a^\dagger_m$ and $a_a$ are creation and annihilation operators, respectively. The index a is used to represent core states and indices m and n indicate excited states.

The quantities $\rho_{ma}$ and $\rho_{mva}$ are single core and valence excitation coefficients and the quantities $\rho_{mnab}$ and
The lowest-order (DHF) and third-order values all also give \( n \). All-order values for 5 are from Ref. [3]. The corresponding reduced oscillator strengths are given in rows labeled \( f \). All-order matrix elements and experimental energies are used in calculation of oscillator strengths.

| \( np \rightarrow n'p \) | 5s – 5p\(_{1/2} \) | 5s – 6p\(_{1/2} \) | 5s – 7p\(_{1/2} \) | 5s – 8p\(_{1/2} \) | 5s – 5p\(_{3/2} \) | 5s – 6p\(_{3/2} \) | 5s – 7p\(_{3/2} \) | 5s – 8p\(_{3/2} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| DHF             | 4.819           | 0.383           | 0.142           | 0.078           | 6.807           | 0.606           | 0.237           | 0.136           |
| Third order     | 4.181           | 0.363           | 0.130           | 0.069           | 5.899           | 0.583           | 0.224           | 0.125           |
| All order       | 4.221           | 0.333           | 0.115           | 0.059           | 5.956           | 0.541           | 0.202           | 0.111           |
| \( f_{5s\rightarrow np} \) | 0.3404          | 0.0040          | 0.0006          | 0.0002          | 0.6905          | 0.0106          | 0.0017          | 0.0006          |
|                  | 6s – 5p\(_{1/2} \) | 6s – 6p\(_{1/2} \) | 6s – 7p\(_{1/2} \) | 6s – 8p\(_{1/2} \) | 6s – 5p\(_{3/2} \) | 6s – 6p\(_{3/2} \) | 6s – 7p\(_{3/2} \) | 6s – 8p\(_{3/2} \) |
| DHF             | 4.256           | 10.286          | 0.976           | 0.375           | 6.187           | 14.457          | 1.409           | 0.597           |
| Third order     | 4.189           | 9.584           | 1.050           | 0.420           | 6.115           | 13.447          | 1.610           | 0.668           |
| All order       | 4.119           | 9.684           | 0.999           | 0.393           | 6.013           | 13.592          | 1.540           | 0.628           |
| \( f_{7s\rightarrow np} \) | -0.1946         | 0.5101          | 0.0117          | 0.0023          | -0.4019         | 1.0267          | 0.0279          | 0.0058          |
|                  | 7s – 5p\(_{1/2} \) | 7s – 6p\(_{1/2} \) | 7s – 7p\(_{1/2} \) | 7s – 8p\(_{1/2} \) | 7s – 5p\(_{3/2} \) | 7s – 6p\(_{3/2} \) | 7s – 7p\(_{3/2} \) | 7s – 8p\(_{3/2} \) |
| DHF             | 0.981           | 9.360           | 17.612          | 1.801           | 1.393           | 13.552          | 24.708          | 2.728           |
| Third order     | 0.952           | 9.304           | 16.679          | 1.944           | 1.347           | 13.517          | 23.349          | 2.943           |
| All order       | 0.954           | 9.189           | 16.844          | 1.865           | 1.352           | 13.353          | 23.587          | 2.833           |
| \( f_{8s\rightarrow np} \) | -0.0190         | -0.3330         | 0.6565          | 0.0186          | -0.0375         | -0.6821         | 1.3170          | 0.0432          |
|                  | 8s – 5p\(_{1/2} \) | 8s – 6p\(_{1/2} \) | 8s – 7p\(_{1/2} \) | 8s – 8p\(_{1/2} \) | 8s – 5p\(_{3/2} \) | 8s – 6p\(_{3/2} \) | 8s – 7p\(_{3/2} \) | 8s – 8p\(_{3/2} \) |
| DHF             | 0.514           | 1.922           | 16.151          | 26.817          | 0.727           | 2.705           | 23.343          | 37.577          |
| Third order     | 0.500           | 1.839           | 16.102          | 25.587          | 0.705           | 2.578           | 23.428          | 35.770          |
| All order       | 0.504           | 1.853           | 15.982          | 25.831          | 0.710           | 2.600           | 23.171          | 36.123          |
| \( f_{9s\rightarrow np} \) | -0.0063         | -0.0278         | -0.4701         | 0.7987          | -0.0124         | -0.0539         | -0.9595         | 1.5993          |

\( \rho_{nnpn} \) are double core and valence excitation coefficients, respectively. We obtain the equations for the excitation coefficients by substituting the above wave function into the many-body Schrödinger equation. The equations are solved iteratively and the resulting expansion coefficients are used to calculate matrix elements. In such a procedure, certain classes of MBPT terms are summed to all orders. However, the restriction of the expansion to the single and double excitations leads to some missing terms in the expression for the matrix elements starting from the fourth order. As it is important to understand how significant higher-order corrections are for the transitions under consideration, we also conduct separate third-order calculation of these matrix elements (including random-phase approximation (RPA) contributions iterated to all orders). The third-order calculation follows that of Ref. [4]. Such a calculation is of lower accuracy than the all-order one but the difference in third-order and all-order values provides an estimate of the importance of the higher-order contributions. Also, the breakdown of both all-order and third-order calculations to different contributions yields information regarding relative importance of the specific terms and possible large cancellations between different terms. Such information can be used to approximate some of the omitted contributions and further estimate the uncertainty of the all-order calculation. We should note that despite the fact that the entire third-order contribution is contained in the all-order result, the extraction of the third-order part from the all-order calculation is not a straightforward task (see Ref. [5] for the correspondence of the terms), so a separate calculation is made to obtain third-order values. The separate calculation also allows us to iterate RPA contribution to all orders.

We use the system of atomic units, a.u., in which \( c, m_e, 4\pi\epsilon_0 \) and the reduced Planck constant \( \hbar \) have the numerical value 1. Polarizability in a.u. has the dimensions of volume, and its numerical values presented here are thus measured in units of \( a_0^3 \), where \( a_0 \approx 0.52918 \) nm is Bohr radius. The atomic units of frequency \( \omega \) is factored out. The atomic unit of frequency \( \omega \) is \( E_h/\hbar \approx 4.1341 \times 10^{16} \) Hz, where \( E_h \) is Hartree energy.

The third-order and all-order results for \( ns \rightarrow n'p \) transitions with \( n, n' = 5, 6, 7 \) and 8 are summarized in Table I together with the lowest-order Dirac-Hartree-Fock (DHF) values. The corresponding reduced oscillator strengths calculated using formula (1) are listed in the rows labeled \( f_{ns\rightarrow np} \). In Eq. (2), \( D \) is the dipole operator and \( \lambda \) is a transition wavelength in nm. The all-order matrix elements and experimental energies from [11] are used in the oscillator strength calculation. The sum of the \( f_{ns\rightarrow np} \) oscillator strengths with \( n = 5, 6, 7, 8 \) slightly exceeds one because the contributions to the sum rule \( \sum_n f_{ns\rightarrow np} = 1 \) from the transitions with \( n = 2, 3, 4 \) are negative.

The results for the \( nd \rightarrow n'p \) matrix elements with \( n = 4, 5, 6 \) and the \( n' = 5, 6, 7, 8 \) and \( 6d \rightarrow 4f \) matrix elements are summarized in Table II. The transitions con-
taining the fine structure components, such as \(ns - 5p_{1/2}\) and \(ns - 5p_{3/2}\) pairs, for example, have very similar relative correlation contributions so we will omit the angular momentum \(j\) subscript in the subsequent discussion. We find that the relative correlation correction contribution varies very significantly with the transition. It is small, below 7\%, for all \(6s - np\), \(7s - np\) and \(8s - np\) transitions and for some \(nd - n'p\) transitions. In those situations where the third order and all-order values differ by less than a few percent we expect the dipole matrix elements to be accurate to at least 2\%.

We should note that in some cases it is possible that such good agreement of the third-order and all-order values is fortuitous and may result from accurate cancellations of the high-order terms. We address this issue below in more detail.

In Ref. [3], the all-order values for the primary transitions were found to agree with a recent high-accuracy measurement \(\mathbf{6}\) to within 0.2\%–0.35\%. The accuracy of the \(5s - 6p\), \(5s - 7p\), and \(5s - 8p\) matrix elements is, however, substantially lower since they are relatively small matrix elements with significant relative correlation contributions. To investigate the correlation contributions in more detail, we give a breakdown of both third-order and all-order calculations for eight selected transitions in Table III. The third-order contributions are separated to random-phase-approximation (RPA), Brueckner-orbital (BO), structural radiation (SR) and normalization (Norm) corrections following Ref. \([9]\). For the all-order contributions, three terms (\(a\), \(c\) and \(d\)) are listed separately and the other 17 terms are grouped together in row labeled “Other”. The derivation and expressions for these terms are given in Refs. [7, 8]. A normalization correction is given in row labeled “Norm”. As it was noted earlier, there is no straightforward correspondence of the all-order and third-order breakdown (full description is given in \([7]\)), but term \(a\) partly corresponds to RPA-like corrections and term \(c\) to BO-like corrections. Term \(d\) is normally small with exception of some transitions. It is quadratic in single-valence excitation coefficients \(\rho_{mv}\) and, therefore, contains only fifth and higher-order terms. We find strong cancellations between BO and RPA terms for \(5s - 6p\), \(5s - 7p\), and \(5s - 8p\) matrix elements. The difficulty of the calculation of such matrix elements has been described before for the case of Cs [3, 12, 13]. However, we also find that term \(d\), which is missing entirely from third-order calculation is relatively large for \(7s - 5p\) and \(7s - 7p\) matrix elements. It is rather puzzling since we observe very good agreement of third-order and all-order results for these transitions. The possible explanation is accurate cancellation of the high-order terms for these transitions. We note that term \(d\) is not significant for the \(6s - 5p\) transition, for which some conclusion of accuracy may be drawn from the comparison with similar Cs transition matrix elements (which are measured to quite good accuracy). Accurate measurements of these matrix elements would be very useful in developing further understanding of this issue. We note that even though this term is significant, it is not very large, on the order of 5\%.

In the case of \(nd - n'p\) transitions, the term \(c\) (or BO term for third-order calculation) dominates. The relative contribution of the correlation correction varies with the transition. For \(5d - 5p\) and \(6d - 6p\) transitions, the DHF approximation gives a very poor result; the sign of the matrix element changes when correlation is added for \(6d - 6p\) matrix elements and the DHF values for \(5d - 5p\) matrix elements are about 7 times too low. As expected,

### Table II: Absolute values of all-order SD electric-dipole matrix elements for the \(np - n'd\) and \(6d - 4f\) transitions in Rb in atomic units. The lowest-order and third-order values all also given. In the cases where lowest order and SD data are of different sign relative signs are shown.

| \(n\) | \(5\) | \(6\) | \(7\) | \(8\) |
|-------|------|------|------|------|
| \(4d_{5/2} - np_{1/2}\) |
| DHF  | 9.046 | 6.725 | 1.181 | 0.578 |
| Third order | 8.092 | 5.289 | 1.119 | 0.566 |
| All order | 7.847 | 4.717 | 1.054 | 0.541 |
| \(4d_{5/2} - np_{3/2}\) |
| DHF  | 4.082 | 2.955 | 0.534 | 0.262 |
| Third order | 3.655 | 2.307 | 0.502 | 0.255 |
| All order | 3.540 | 2.055 | 0.470 | 0.242 |
| \(5d_{5/2} - np_{1/2}\) |
| DHF  | 12.241 | 8.829 | 1.601 | 0.787 |
| Third order | 10.964 | 6.915 | 1.505 | 0.764 |
| All order | 10.634 | 6.184 | 1.411 | 0.726 |
| \(5d_{5/2} - np_{3/2}\) |
| DHF  | 0.244 | 18.701 | 13.639 | 2.660 |
| Third order | 1.220 | 18.241 | 10.600 | 2.573 |
| All order | 1.616 | 18.106 | 9.768 | 2.400 |
| \(6d_{5/2} - np_{1/2}\) |
| DHF  | 0.512 | -0.254 | 31.349 | 22.584 |
| Third order | 1.076 | 1.375 | 31.563 | 17.647 |
| All order | 1.180 | 1.989 | 31.422 | 16.631 |
| \(6d_{5/2} - np_{3/2}\) |
| DHF  | 0.255 | -0.028 | 14.158 | 9.901 |
| Third order | 0.513 | 0.732 | 14.242 | 7.662 |
| All order | 0.558 | 1.012 | 14.161 | 7.215 |
| \(6d_{5/2} - 4f_{5/2}\) |
| DHF  | 0.778 | -0.047 | 42.500 | 29.603 |
| Third order | 1.532 | 2.184 | 42.709 | 23.041 |
| All order | 1.658 | 2.947 | 42.481 | 21.784 |

In Ref. [3], the all-order values for the primary transitions were found to agree with a recent high-accuracy measurement \(\mathbf{6}\) to within 0.2\%–0.35\%. The accuracy of the \(5s - 6p\), \(5s - 7p\), and \(5s - 8p\) matrix elements is, however, substantially lower since they are relatively small matrix elements with significant relative correlation contributions. To investigate the correlation contributions in more detail, we give a breakdown of both third-order and all-order calculations for eight selected transitions in Table III. The third-order contributions are separated to random-phase-approximation (RPA), Brueckner-orbital (BO), structural radiation (SR) and normalization (Norm) corrections following Ref. \([9]\). For the all-order contributions, three terms (\(a\), \(c\) and \(d\)) are listed separately and the other 17 terms are grouped together in row labeled “Other”. The derivation and expressions for these terms are given in Refs. [7, 8]. A normalization correction is given in row labeled “Norm”. As it was noted earlier, there is no straightforward correspondence of the all-order and third-order breakdown (full description is given in \([7]\)), but term \(a\) partly corresponds to RPA-like corrections and term \(c\) to BO-like corrections. Term \(d\) is normally small with exception of some transitions. It is quadratic in single-valence excitation coefficients \(\rho_{mv}\) and, therefore, contains only fifth and higher-order terms. We find strong cancellations between BO and RPA terms for \(5s - 6p\), \(5s - 7p\), and \(5s - 8p\) matrix elements. The difficulty of the calculation of such matrix elements has been described before for the case of Cs [3, 12, 13]. However, we also find that term \(d\), which is missing entirely from third-order calculation is relatively large for \(7s - 5p\) and \(7s - 7p\) matrix elements. It is rather puzzling since we observe very good agreement of third-order and all-order results for these transitions. The possible explanation is accurate cancellation of the high-order terms for these transitions. We note that term \(d\) is not significant for the \(6s - 5p\) transition, for which some conclusion of accuracy may be drawn from the comparison with similar Cs transition matrix elements (which are measured to quite good accuracy). Accurate measurements of these matrix elements would be very useful in developing further understanding of this issue. We note that even though this term is significant, it is not very large, on the order of 5\%.

In the case of \(nd - n'p\) transitions, the term \(c\) (or BO term for third-order calculation) dominates. The relative contribution of the correlation correction varies with the transition. For \(5d - 5p\) and \(6d - 6p\) transitions, the DHF approximation gives a very poor result; the sign of the matrix element changes when correlation is added for \(6d - 6p\) matrix elements and the DHF values for \(5d - 5p\) matrix elements are about 7 times too low. As expected,
TABLE III: Contributions to third-order and all-order electric-dipole reduced matrix elements (a.u.) for selected transitions in Rb.

| 5s − 5p_{1/2} | 5s − 7p_{1/2} | 7s − 5p_{1/2} | 7s − 7p_{1/2} | 5d_{3/2} − 5p_{1/2} | 5d_{3/2} − 7p_{1/2} | 6d_{3/2} − 5p_{1/2} | 6d_{3/2} − 4f_{5/2} |
|----------------|----------------|----------------|----------------|---------------------|---------------------|---------------------|---------------------|
| Third order    |                |                |                |                     |                     |                     |                     |
| DHF           | 4.819          | 0.149          | 0.981          | 17.612              | 0.244               | 13.639              | -0.254              | 6.109               |
| RPA           | -0.213         | -0.060         | 0.015          | -0.024              | 0.101               | 0.030               | 0.045               | 0.002               |
| BO            | -0.419         | 0.040          | -0.038         | -0.899              | 0.888               | -3.048              | 1.589               | 3.041               |
| SR            | 0.027          | 0.009          | -0.004         | 0.002               | -0.013              | -0.004              | -0.005              | 0.001               |
| Norm          | -0.033         | -0.001         | -0.002         | -0.012              | -0.001              | -0.016              | 0.000               | -0.004              |
| Total         | 4.181          | 0.130          | 0.952          | 16.679              | 1.220               | 10.600              | 1.375               | 9.150               |
| All order     |                |                |                |                     |                     |                     |                     |                     |
| DHF           | 4.819          | 0.142          | 0.981          | 17.612              | 0.244               | 13.639              | -0.254              | 6.109               |
| Term a        | -0.234         | -0.064         | 0.014          | -0.025              | 0.102               | 0.036               | 0.047               | 0.005               |
| Term c        | -0.375         | 0.009          | -0.077         | -0.648              | 1.575               | -3.372              | 2.752               | 4.393               |
| Term d        | 0.039          | 0.017          | 0.056          | 0.149               | -0.197              | -0.024              | -0.439              | -0.089              |
| Other         | 0.039          | 0.012          | -0.006         | 0.005               | -0.025              | -0.004              | -0.009              | -0.002              |
| Norm          | -0.068         | -0.002         | -0.014         | -0.248              | -0.083              | -0.506              | -0.109              | -0.483              |
| Total         | 4.220          | 0.115          | 0.954          | 16.844              | 1.616               | 9.768               | 1.989               | 9.938               |

we find very large, 25% − 30%, differences between third-order and all-order calculations for these transitions as the all-order calculation includes correlation more completely. The term c can be corrected by including triple excitations or use of the semi-empirical scaling described in Refs. [3, 7, 12]. To check the validity of the scaling approach, we applied such a method to the 5d − 5p matrix elements and compared the resulting ratio with the experimental measurement [14].

TABLE IV: The ratio of the experimental and corresponding theoretical values from Ref. [14] was obtained using relativistic third-order many-body theory [2]; some higher-order Brueckner-orbital terms were also included, which accounts for the difference with our third-order result. As noted above, the largest contribution to the 5p − 5d matrix elements calculated using the all-order method comes from the term c containing single-valence excitation coefficients $\rho_{mv}$. We scale these excitation coefficients $\rho_{mv}$ with the ratio of the experimental and corresponding theoretical correlation energies as described in Refs. [14, 12]. We list the results obtained using such scaling in a row labeled “Scaled”. We find very significant differences between all high-precision calculations, which indicates that the accuracy of the all-order calculation is around 10-20% for these matrix elements. However, our all-order result for the ratio $R$ is in much better agreement with experiment [14] than the third-order value and theoretical calculation of Ref. [14].

III. LIFETIMES

We use the resulting all-order matrix elements to calculate the lifetimes of the 6s, 7s, 8s, 6p, 7p, 8p, 4d, 5d, and 6d levels in Rb for the comparison with experiment and providing benchmark values for these lifetimes.

The Einstein A-coefficients $A_{vw}$ [10] are calculated using the formula

$$A_{vw} = \frac{2.02613 \times 10^{15} \left|\langle v|D|w\rangle\right|^2}{\lambda^3 \left(2\nu + 1\right)} \text{ s}^{-1},$$

where $\langle v|D|w\rangle$ is the reduced electric-dipole matrix element for the transition between states $v$ and $w$ and $\lambda$ is corresponding wavelength in nm. The lifetime of the
state $v$ is calculated as

$$\tau_v = \frac{1}{\sum_w A_{vw}}$$  \hspace{1cm} (4)

and the denominator of Eq. (1) gives the radiative width of the level $v$.

### TABLE V: Transition energies ($E/hc$) in cm$^{-1}$, matrix elements (in a.u.) and corresponding contributions to $7p_{3/2}$ radiative width (in MHz).

| Transition $(vw)$ | $(v||D||w)$ | $\delta E_{vw}$ | $A_{vw}$ | $\sum_w A_{vw}$ |
|------------------|--------------|-----------------|----------|-----------------|
| $7p_{3/2} - 7s$  | 23.587       | 1559            | 1.068    | 1.068           |
| $7p_{3/2} - 6s$  | 1.540        | 7736            | 0.556    | 1.624           |
| $7p_{3/2} - 5s$  | 0.202        | 27870           | 0.447    | 2.071           |
| $7p_{3/2} - 5d_{3/2}$ | 4.242      | 2169            | 0.093    | 2.164           |
| $7p_{3/2} - 4d_{5/2}$ | 0.470      | 8515            | 0.069    | 2.234           |
| $7p_{3/2} - 5d_{5/2}$ | 12.798     | 2169            | 0.847    | 3.081           |
| $7p_{3/2} - 4d_{5/2}$ | 1.411      | 8515            | 0.623    | 3.703           |

Several electric-dipole (E1) transitions contribute to the lifetime of each of the levels considered here. The simplest case is that of the 6s level, where only 6s - 5p$_{1/2}$ and 6s - 5p$_{3/2}$ transitions need to be included. To calculate the lifetime of the 5p$_{1/2}$ state, we need to include ten E1 transitions and in the case of the 6d$_{3/2}$ level seven E1 transitions are allowed, including the 6d$_{3/2} - 4f_{5/2}$ transition. The experimental energies from [11] are used in the lifetime calculation. We illustrate the importance of the different channels contributing to the lifetime of the 7p$_{3/2}$ state in Table V, where we give the coefficients $A_{vw}$ for each transition together with the transition energies from [11] and corresponding matrix elements from Tables II. The accumulated sum $\sum_w A_{vw}$ is listed in the last column. We find the contribution from the $7p_{3/2} - 5d_{5/2}$ transition to be nearly as large as the contribution from the $7p_{3/2} - 7s$ transition. All seven contributions need to be included in an accurate calculation. The smallest contribution to $\sum_w A_{vw}$ comes from $7p_{3/2} - 4d_{3/2}$ transition and is around 2%.

We list the contributions to 6d$_{3/2}$ and 6d$_{5/2}$ lifetimes as well as the corresponding matrix elements and transition energies in Table VI. The dominant contributions to 6d$_{3/2}$ and 6d$_{5/2}$ lifetimes come from the 6d$_{3/2} - 5p_{1/2}$ and 6d$_{5/2} - 5p_{3/2}$ transitions, respectively. The next largest contribution is 14% for the 6d$_{1/2}$ lifetime and 7% for the 6d$_{5/2}$ lifetime. We find the contributions from $6d_{3/2} - 4f_{5/2}$ and $6d_{5/2} - 4f_{7/2}$ transitions to be around 7% for the corresponding level.

The results for the 8s, 8p and 8d levels obtained using all-order matrix elements are compared with experimental values from Refs. [12, 13] in Table VII. We omit the effect of the blackbody radiation in our calculations. In Ref. [12], it was estimated to be small for the levels considered here with the exception of the 8p levels. It is still far below experimental uncertainty of the 8p level lifetime. The results agree with experiment within the experimental precision for 6s, 7s, 8s, 6p, and 4d levels. The values of the 7p, 8p, 5d, and 6d lifetimes are in good agreement with experiment. The lower accuracy of the calculations is expected for these levels owing to the lower accuracy of the $np - n'd$ matrix elements with comparison to most of the $np - n's$ ones due to large correlation corrections for these matrix elements. It should be noted that the experimental uncertainties of 7p, 8p, and 5d lifetimes are rather large (up to 20%) and two recent experiments for the 6d$_{3/2}$ level give substantially

### TABLE VI: Transition energies $E/hc$ in cm$^{-1}$, matrix elements (in a.u.) and the corresponding contributions to 6d$_{3/2}$ and 6d$_{5/2}$ radiative widths (in MHz).

| Transition $(vw)$ | $(v||D||w)$ | $\delta E_{vw}$ | $A_{vw}$ | $\sum_w A_{vw}$ |
|------------------|--------------|-----------------|----------|-----------------|
| 6d$_{3/2} - 5p_{1/2}$ | 1.380        | 16108           | 2.948    | 2.948           |
| 6d$_{3/2} - 6p_{1/2}$ | 1.989        | 4972            | 0.246    | 3.194           |
| 6d$_{3/2} - 7p_{1/2}$ | 31.422       | 852             | 0.309    | 3.504           |
| 6d$_{3/2} - 5p_{3/2}$ | 0.558        | 15870           | 0.630    | 4.134           |
| 6d$_{3/2} - 6p_{3/2}$ | 1.012        | 4894            | 0.061    | 4.195           |
| 6d$_{3/2} - 7p_{3/2}$ | 14.161       | 817             | 0.055    | 4.250           |
| 6d$_{3/2} - 4f_{5/2}$ | 9.938        | 1895            | 0.341    | 4.591           |
| 6d$_{3/2} - 5p_{5/2}$ | 1.658        | 15872           | 3.712    | 3.712           |
| 6d$_{5/2} - 6p_{1/2}$ | 2.974        | 4896            | 0.351    | 4.063           |
| 6d$_{5/2} - 7p_{1/2}$ | 42.481       | 819             | 0.335    | 4.398           |
| 6d$_{5/2} - 5p_{3/2}$ | 2.642        | 1897            | 0.016    | 4.414           |
| 6d$_{5/2} - 4f_{5/2}$ | 11.813       | 1897            | 0.322    | 4.736           |

### TABLE VII: Radiative widths (MHz) and lifetimes (in ns) for ns, np, and nd states in Rb. Experimental values are taken from the compilation in Ref. [13] unless noted otherwise. The lifetimes obtained using ab initio all-order matrix elements and scaled all-order values are listed in columns $\tau_v$ and $\tau_v^{exp}$, respectively.

| State | $\sum_w A_{vw}$ | $\tau_v$ | $\tau_v^{sc}$ | $\tau_v^{exp}$ |
|-------|------------------|----------|---------------|---------------|
| 6s    | 21.761           | 46.0     | 45.4          | 46.5          |
| 7s    | 11.318           | 88.4     | 88.3          | 88.6          |
| 8s    | 6.201            | 161.3    | 161.8         | 161(3)        |
| 6p$_{1/2}$ | 7.729          | 129      | 123           | 125(4)        |
| 7p$_{1/2}$ | 3.394           | 295      | 280           | 272(15)       |
| 8p$_{1/2}$ | 1.899           | 527      | 508           | 154(7)        |
| 6p$_{3/2}$ | 8.461           | 118      | 113           | 112(3)        |
| 7p$_{3/2}$ | 3.703           | 270      | 258           | 246(10)       |
| 8p$_{3/2}$ | 2.056           | 486      | 471           | 400(80)       |
| 4d$_{5/2}$ | 11.478          | 87       | 83.5          | 86(6)         |
| 5d$_{5/2}$ | 5.193           | 193      | 243           | 205(40)       |
| 6d$_{3/2}$ | 4.591           | 218      | 263           | 256(4)        |
| 4d$_{5/2}$ | 10.674          | 94       | 90            | 94(6)         |
| 5d$_{5/2}$ | 5.340           | 187      | 235           | 230(23)       |
| 6d$_{5/2}$ | 4.736           | 211      | 252           | 249(5)        |
different values: 256(4) ns and 298(8) ns. Our result for 6d_{3/2} lifetime (263 ns) is very close to the first measurement, however, large uncertainties in the correlation contributions to the relevant transitions do not allow to rule out 10% larger value of this lifetime.

The accuracy of the theoretical calculations for these levels may be improved by including some triple-excitation contributions into the corresponding wave functions.

We estimate some omitted higher-order contributions using the scaling of the single excitation coefficients \( \rho_{mn} \) described above. The contributions containing these single-excitation coefficients are dominant for all of the transitions needed for the calculation of lifetimes in Table VII. The lifetimes obtained using scaled all-order matrix elements are listed in column \( \tau_\text{vac}^{\text{ex}} \). We find that the scaled data agree with experimental values within the experimental uncertainty for all levels with exception of \( 7p_{3/2} \) and \( 6d_{3/2} \), where the theoretical values are just outside the experimental uncertainties.

### IV. POLARIZABILITIES

The valence part of the ac polarizability of an alkali-metal atom in \( ns \) state can be calculated using the formula

\[
\alpha_{n's}^{\text{a}}(\omega) = \frac{1}{3} \sum_{\omega'} \left( \frac{(E_{n'p_{1/2}} - E_{ns})(n'p_{1/2}\|D\|ns)^2}{(E_{n'p_{1/2}} - E_{ns})^2 - \omega^2} + \frac{(E_{n'p_{3/2}} - E_{ns})(n'p_{3/2}\|D\|ns)^2}{(E_{n'p_{3/2}} - E_{ns})^2 - \omega^2} \right), \tag{5}
\]

where \( D \) is the dipole operator. In this formula, \( \omega \) is assumed to be at least several linewidths off resonance with the corresponding transition.

The core contribution to the polarizability, calculated in the DHF approximation is found to be small for Rb (9.3 \( a_0^3 \)) and is weakly dependent on \( \omega \) in the frequency range considered here. The static value for the polarizability of Rb\(^+\) calculated in the random-phase approximation (RPA) \[16\] \[17\] is 9.1 \( a_0^3 \) close to the value of 9.0 \( a_0^3 \) obtained by Johansson \[18\] from analysis of the observed term values of nonpenetrating Rydberg states. The accuracy of the RPA approximation for the core polarizability is estimated to be 5 \% in Ref. \[8\]. We use the RPA value for the core polarizability of Rb\(^+\) as a baseline, and adjust it to account for valence electron using Eq. (4) with \( n' = 2, 3, 4 \) and the frequency dependence by using DHF calculations. The RPA and DHF values differ by only 2 \%. The correction to the core polarizability owing to the presence of the valence electron is very small, it is only \(-0.3 a_0^3\) for 5s state in DHF approximation.

First, we describe the calculation of the ground state polarizability, \( \alpha_{5s}(\omega) \). The expression \[19\] converges rapidly with \( n' \) so the contribution with \( n' = 5 \) is dominant. We use experimental 5s – 5p matrix elements from \[8\], all-order matrix elements from Ref. \[8\], and experimental energies from \[11\] to evaluate the expression of Eq. (5) with \( n' = 5, 6, 7, 8 \). The contribution to the ground state polarizability from states with \( n' > 8 \) is very small, 0.2\( a_0^3 \) in DHF approximation. We plot the ground state frequency-dependent polarizability in the vicinity of the 5s – 5p_{1/2} and 5s – 5p_{3/2} resonances in Fig. 1. The behavior within the few linewidths from the resonances is not shown and the exact placement of the resonances is indicated by the vertical dashed lines. As we see from Fig. 1 \( \alpha_{5s}(\omega) \) changes sign between two resonances. We determined that \( \alpha_{5s}(\omega) = 0 \) at \( \lambda_{vac} = 790.032(8) \) nm \[2\], where the uncertainty results from the uncertainty of the polarizability calculation. This crossing point is of interest for the optical lattice experiments with Rb as the atoms will no longer be trapped at this wavelength.

We give the breakdown of the different contributions to the ground state polarizability for one particular frequency, \( \omega = 0.04298 \) a.u., corresponding to \( \lambda = 1.06 \mu m \) \[19\], in Table VII. The comparison with other theory \[20\] and experiment \[21\] is also given. Our value is in good agreement with the result from \[21\]. The discrepancy is due to our use of more accurate values for the electric-dipole matrix elements. Our result is just outside the range of uncertainty of the value \( \alpha = 769 \pm 61 \) \( a_0^3 \) inferred by Bonin and Kadar-Kallen from an atomic deflection experiment \[21\].

Next, we describe the calculation of the polarizabilities of the Rydberg states. We calculate the polarizabilities of the \( ns \) states of Rb with \( n = 8 \ldots 19 \) using the DHF approximation; i.e. using DHF values for both energies and matrix elements in Eq. \[5\]. The summation over \( n' \) in Eq. \[4\] is truncated at \( n' = 23 \). The DHF calculations are done on the non-linear grid of the form

\[
r(i) = r_0(e^{(i-1)h} - 1).
\]

To calculate matrix elements and energies of the first few
TABLE VIII: Contributions to ground state dynamic polarizability of Rb in $a_0^3$ for $\omega = 0.04298$ a.u.

| Contribution | Value |
|--------------|-------|
| $n' = 5$ | 682.84 |
| $n' = 6$ | 1.48 |
| $n' = 7$ | 0.16 |
| $n' = 8$ | 0.04 |

$\alpha_v (n' = 5..8) = 684.52(72)$

$\alpha_v (n' > 8) = 0.17(8)$

$\alpha_{vc} (n' = 2..4) = -0.26(13)$

$\alpha = 9.10(45)$

Final $\alpha = 693.5(9)$

Ref. [20] 711.4

Expt. [21] 769(61)

TABLE IX: Dynamic polarizabilities $\alpha_{ns}(\omega)$ (in units of $a_0^3$) for Rb, $\omega = 0.0576645$ a.u., i.e. $\lambda = 790$ nm.

| n | $\alpha_{DHF}$ | $\alpha_{ex}$ |
|---|---|---|
| 8 | -304 | -295$^a$ |
| 9 | -292 | 15 | -285 |
| 10 | -289 | 16 | -284 |
| 11 | -288 | 17 | -282 |
| 12 | -287 | 18 | -280 |
| 13 | -287 | 19 | -277 |

$^a$High-accuracy value obtained using experimental energies and all-order matrix elements for the dominant terms with $n' = 7, 8$.

V. CONCLUSION

We have conducted a systematic study of the $ns - n'p$ and $nd - n'p$ electric-dipole matrix elements in rubidium using relativistic all-order method. An investigation of the accuracy of these matrix elements was performed. The resulting matrix elements were used to calculate lifetimes of the $ns$ and $np$ levels with $n = 6, 7, 8$ and $nd$ levels with $n = 4, 5, 6$. The lifetime values were found to be in good agreement with experiment. The dynamic polarizabilities of the $ns$ Rb states, which are of interest for the optimization of quantum computation scheme with neutral atoms mediated by the conditional excitations to Rydberg states, were also calculated.

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