# Relativistic configuration-interaction oscillator strengths for lowest $E1$ transitions in silver and gold isoelectronic sequences

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Relativistic oscillator strengths are computed for $ns_{1/2}$-$np_{1/2,3/2}$ transitions in silver and gold isoelectronic sequences employing configuration-interaction method with numerical Dirac-Fock wave functions generated with noninteger outermost core shell occupation number. This method is optimized to represent efficiently the core-valence electron correlation that is known to be important for transitions under consideration. The presented results are compared with our earlier data computed with core-valence correlation represented in the semiclassical core polarization picture within single configuration Dirac-Fock scheme as well as available experimental values.

## I. INTRODUCTION

As it has been demonstrated almost 30 years ago, the inclusion of core-valence electron correlation is important in calculating oscillator strengths for *ns-np* transitions not only for alkalis but also for noble metals. However in those days the only way to include this effect within fully relativistic Dirac-Fock scheme (since simultaneous inclusion of relativistic effects was also crucial) was to treat it in the semiclassical core polarization picture using an appropriate model potential depending, however, on arbitrary chosen or empirically adjusted parameters. Such approach turned out to be very successful for many systems among them silver and gold isoelectronic sequences [1,2]. Even now the accurate representation of valence-core electron correlation influence on oscillator strengths within the multiconfiguration Dirac-Fock (MCDF) or configuration-interaction Dirac-Fock (CIDF) scheme poses a very difficult task requiring hundreds of thousand of configurations to be included as too many of them possess roughly equal contributions. This is acceptable for calculations of single transition but it is impossible if numerous transitions have to be studied. In the past few years we have undertaken the task to improve the efficiency of configuration-interaction (CI) scheme through the different modifications of the way the spin orbitals used to construct the CI wave function are generated. It is, thus, our hope to improve accuracy of CI scheme by a proper choice of correlating spin orbitals, which would allow us to obtain reasonably accurate results even with basis sets which, for obvious reasons, are far from being complete.

In our previous papers [3,4], we presented an idea to improve the ability of the CI scheme to represent core-valence electron correlations. It is based on assumption that core-valence correlations mostly affect the outermost shell of the core. We assume that this effect may be represented in the single configuration Dirac-Fock scheme as a change in effective occupation number of outermost core shell which becomes a noninteger, similar to a multiconfiguration scheme

where the square of the configuration mixing coefficient multiplied by integer occupation number can be treated as effective noninteger occupation number. The relativistic wave functions used for CI expansion are generated in the single configuration Dirac-Fock calculations with noninteger occupation number $2(2l+1)q$ of the outermost core shell. The $q$ parameter is determined through minimization of the total CI energy of the state considered $[\text{CIDF}(q)]$.

In our previous papers [3,4], we had demonstrated that this method works well also for $ns^2$-$nsnp$ $^1P_1, ^3P_1$ spin al-

TABLE I. Values of $q$ parameter in Ag isoelectronic sequence.

| System | States | $q$ |
|---|---|---|
| Ag | $^2P_{1/2}$ | 0.641 |
| | $^2P_{3/2}$ | 0.664 |
| Cd$^+$ | $^2P_{1/2}$ | 0.598 |
| | $^2P_{3/2}$ | 0.601 |
| In$^{2+}$ | $^2P_{1/2}$ | 0.565 |
| | $^2P_{3/2}$ | 0.567 |
| Sn$^{3+}$ | $^2P_{1/2}$ | 0.529 |
| | $^2P_{3/2}$ | 0.529 |
| Sb$^{4+}$ | $^2P_{1/2}$ | 0.505 |
| | $^2P_{3/2}$ | 0.501 |
| Te$^{5+}$ | $^2P_{1/2}$ | 0.509 |
| | $^2P_{3/2}$ | 0.494 |
| I$^{6+}$ | $^2P_{1/2}$ | 0.866 |
| | $^2P_{3/2}$ | 0.867 |
| Xe$^{7+}$ | $^2P_{1/2}$ | 0.897 |
| | $^2P_{3/2}$ | 0.898 |
| Cs$^{8+}$ | $^2P_{1/2}$ | 0.919 |
| | $^2P_{3/2}$ | 0.899 |
| Ba$^{9+}$ | $^2P_{1/2}$ | 0.925 |
| | $^2P_{3/2}$ | 0.923 |
| La$^{10+}$ | $^2P_{1/2}$ | 0.941 |
| | $^2P_{3/2}$ | 0.940 |

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TABLE II. Values of $q$ parameter in Au isoelectronic sequence.

| System | States | $q$ |
|---|---|---|
| Au | $^2P_{1/2}$ | 0.635 |
| | $^2P_{3/2}$ | 0.667 |
| Hg$^+$ | $^2P_{1/2}$ | 0.581 |
| | $^2P_{3/2}$ | 0.589 |
| Tl$^{2+}$ | $^2P_{1/2}$ | 0.523 |
| | $^2P_{3/2}$ | 0.542 |
| Pb$^{3+}$ | $^2P_{1/2}$ | 0.481 |
| | $^2P_{3/2}$ | 0.503 |
| Bi$^{4+}$ | $^2P_{1/2}$ | 0.443 |
| | $^2P_{3/2}$ | 0.464 |

lowed and spin-forbidden transitions in neutral Sr, Ba, Zn, Cd, Hg, and Yb as well as in Cd I and Hg I isoelectronic sequences. Moreover our recent unpublished data for $7s_{1/2}$ $-7p_{1/2,3/2}$ transitions in Fr I (0.334 and 0.776, respectively) obtained with method presented above are in good agreement with both experiment and with probably the most accurate theoretical many-body perturbative treatment (MBPT) data. Therefore, we believe that this method can be successful in cases when the core-valence correlations domi-

TABLE III. Transition energies in a.u. for $5s\ ^2S_{1/2}-5p\ ^2P_{1/2}$, $^2P_{3/2}$ in Ag isoelectronic sequence. For description of theoretical methods, see text.

| System | Transition | CIDF | CIDF($q$) | Experiment[a] |
|---|---|---|---|---|
| Ag | $^2S_{1/2}-^2P_{1/2}$ | 0.111874 | 0.134194 | 0.134649 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.114625 | 0.136576 | 0.138844 |
| Cd$^+$ | $^2S_{1/2}-^2P_{1/2}$ | 0.184024 | 0.200564 | 0.201099 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.193381 | 0.210862 | 0.212410 |
| In$^{2+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.246672 | 0.259907 | 0.260536 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.264238 | 0.278347 | 0.280320 |
| Sn$^{3+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.306091 | 0.316477 | 0.316956 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.333364 | 0.344459 | 0.346611 |
| Sb$^{4+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.364205 | 0.371465 | 0.371642 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.402729 | 0.410454 | 0.412590 |
| Te$^{5+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.420902 | 0.425550 | 0.425270 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.472227 | 0.477096 | 0.479099 |
| I$^{6+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.475914 | 0.478572 | 0.478233 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.541644 | 0.544368 | 0.546578 |
| Xe$^{7+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.529709 | 0.531249 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.611573 | 0.613123 | |
| Cs$^{8+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.582807 | 0.583730 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.682673 | 0.683823 | |
| Ba$^{9+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.635536 | 0.636214 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.755411 | 0.756083 | |
| La$^{10+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.688104 | 0.688542 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.830136 | 0.830536 | |

[a]Reference [6].

TABLE IV. Transition energies in a.u. for $6s\ ^2S_{1/2}-6p\ ^2P_{1/2}$, $^2P_{3/2}$ in Au isoelectronic sequence.

| System | Transition | CIDF | CIDF($q$) | Experiment[a] |
|---|---|---|---|---|
| Au | $^2S_{1/2}-^2P_{1/2}$ | 0.146341 | 0.171718 | 0.170220 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.159468 | 0.186348 | 0.187604 |
| Hg$^+$ | $^2S_{1/2}-^2P_{1/2}$ | 0.216362 | 0.236211 | 0.234583 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.251914 | 0.275411 | 0.276150 |
| Tl$^{2+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.277850 | 0.294792 | 0.292321 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.338815 | 0.358771 | 0.359814 |
| Pb$^{3+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.336133 | 0.350136 | 0.347001 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.425499 | 0.441886 | 0.442962 |
| Bi$^{4+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.392452 | 0.403747 | 0.399837 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.513068 | 0.526166 | 0.527050 |

[a]Reference [6].

nates oscillator strength calculations or at least is very important.

## II. CALCULATIONS AND RESULTS

Calculations are performed in the following seven steps:

1. The core spin orbitals are generated with the usual single configuration Dirac-Fock method [5] for the ground state of the system under consideration.

2. Both occupied and virtual spin-orbitals are generated in the single configuration Dirac-Fock approach with noninteger occupation number $2(2l+1)q$ of the outermost shell with given value of $q$.

3. Construction the CI wave function of the system.

4. Diagonalization of the full relativistic Hamiltonian.

5. Adjustment of $q$ to minimize the total multiconfiguration energy of the system for a given $^{2S+1}L_J$ state (so-called optimal level-OL scheme), usually the upper state of the transition and final value of $q$ is later used also for the lower state in order to exclude the nonorthogonality problems.

6. Steps 2–5 are repeated until minimization is achieved with accuracy for the total energy better than $10^{-5}$ a.u.

7. Calculation of oscillator strength for transition considered.

Calculation were performed for $ns_{1/2}$-$np_{1/2,3/2}$ transitions in the silver isoelectronic sequence (through La$^{10+}$) and gold isoelectronic sequence (through Bi$^{4+}$). As can be seen from Tables I and II the resulting values of $q$ vary between 0.44 and 0.94 with $q=1$ corresponding to integer occupation of the $d^{10}$ shell of the core. For the higher ionization stages in the silver isoelectronic sequence the value of $q$ approaches 1 as the core-valence correlation diminishes in comparison with Coulomb field. In order to account properly for valence-core correlation we had to include in the basis set configurations with excitations leading to the split $d^{10}$ shell (i.e., containing $d^9$ and $d^8$ shell).

The basis consists of spin orbitals: $5s\ 5p\ 5d\ 4f\ 6s\ 6p\ 6d$ $7s\ 7p\ 7d$ for Ag and $6s\ 6p\ 6d\ 5f\ 7s\ 7p\ 7d\ 8s\ 8p\ 8d$ for Au system. The single and double excitations have been included in CI calculations. However the double excitations are limited only to configurations such as: {5snl}, {5pnl}, and

TABLE V. Oscillator strengths for $5s\ ^2S_{1/2}-5p\ ^2P_{1/2}, ^2P_{3/2}$ in Ag isoelectronic sequence.

| System | Transition | CIDF | CIDF($q$) | DF+CP [a] | Experiment[b] |
|--------|-----------|------|-----------|-----------|---------------|
| Ag | $^2S_{1/2}-^2P_{1/2}$ | 0.308 | 0.242 | 0.223 | 0.22, 0.20,0.23 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.625 | 0.495 | 0.462 | 0.45, 0.46, 0.48 |
| Cd$^+$ | $^2S_{1/2}-^2P_{1/2}$ | 0.319 | 0.253 | 0.232 | 0.21, 0.19,0.22 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.670 | 0.536 | 0.497 | 0.46, 0.40, 0.51 |
| In$^{2+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.320 | 0.257 | 0.237 | 0.27, 0.28 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.685 | 0.555 | 0.518 | 0.60, 0.53 |
| Sn$^{3+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.307 | 0.258 | 0.243 | 0.26 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.671 | 0.567 | 0.538 | 0.56, 0.64 |
| Sb$^{4+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.282 | 0.256 | 0.245 | 0.26 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.628 | 0.572 | 0.551 | 0.59 |
| Te$^{5+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.257 | 0.251 | 0.247 | 0.21 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.584 | 0.573 | 0.565 | 0.47 |
| I$^{6+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.242 | 0.226 | 0.245 | 0.25 |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.557 | 0.523 | 0.567 | 0.57 |
| Xe$^{7+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.232 | 0.223 | 0.242 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.543 | 0.522 | 0.569 | |
| Cs$^{8+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.225 | 0.219 | 0.244 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.536 | 0.521 | 0.582 | |
| Ba$^{9+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.220 | 0.216 | 0.244 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.531 | 0.522 | 0.592 | |
| La$^{10+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.216 | 0.213 | 0.239 | |
| | $^2S_{1/2}-^2P_{3/2}$ | 0.529 | 0.522 | 0.588 | |

[a]Reference [2].
[b]References for experimental data quoted in [2].

{$5dnl$} for Ag or {$6snl$}, {$6pnl$}, and {$6dnl$} for Au. That is, that one electron has been excited from the outermost core shell to the next open shell. We believe that these configurations are the most appropriate to represent core-valence correlations. In addition, we also considered triple excited configurations: $5p^3$, $5p5s^2$, and $5p^25s$ for Ag or $6p^3$, $6p6s^2$, $6p^26s$ for Au system accompanying the $d^8$ shell.

Transition energies were computed as differences of total energies of proper $^{2S+1}L_J$ states which included the Breit in-

teraction as a first order perturbation corrections evaluated with many-electron wave function. Oscillator strengths were computed in the Babushkin gauge using theoretical transition energies.

In order to assess the effect of $q$ parameter on transition energies and oscillator strengths additional computations were performed for each system using the same basis set as employed for noninteger occupation number calculations but
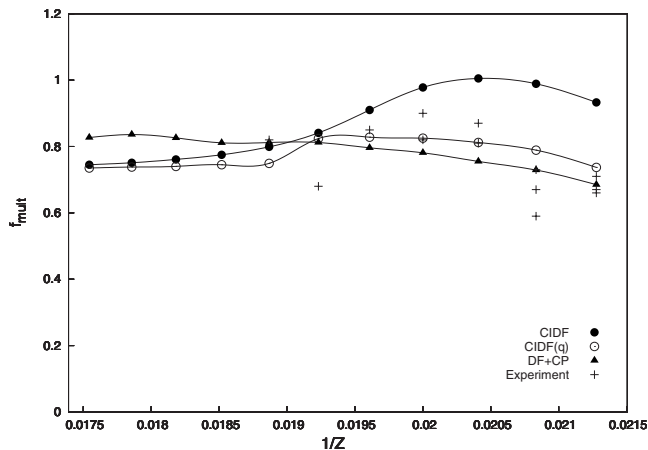


FIG. 1. Oscillator strengths for $5s\ ^2S-5p\ ^2P$ multiplet transitions in silver isoelectronic sequence. For description of theoretical methods, see text.
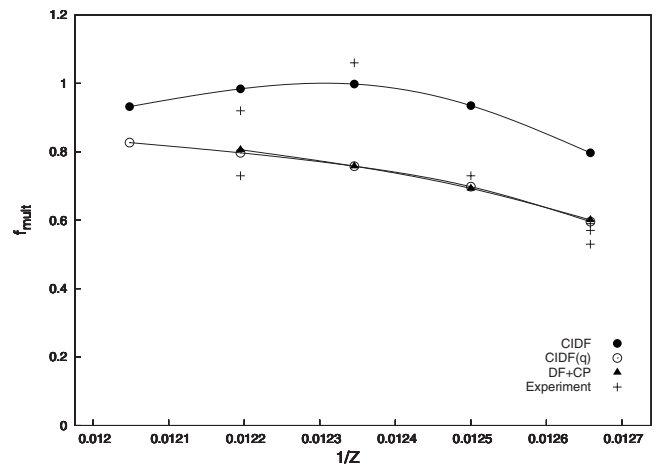


FIG. 2. Oscillator strengths for $6s\ ^2S-6p\ ^2P$ multiplet transitions in gold isoelectronic sequence. For description of theoretical methods, see text.

TABLE VI. Oscillator strengths for $6s\ ^2S_{1/2}-6p\ ^2P_{1/2},\ ^2P_{3/2}$ in Au isoelectronic sequence.

| System | Transition | CIDF | CIDF($q$) | DF+CP [a] | Experiment[b] |
|---|---|---|---|---|---|
| Au | $^2S_{1/2}-^2P_{1/2}$ | 0.262 | 0.189 | 0.183 | 0.19, 0.18 |
|  | $^2S_{1/2}-^2P_{3/2}$ | 0.535 | 0.407 | 0.418 | 0.41, 0.39,0.351 |
| Hg$^+$ | $^2S_{1/2}-^2P_{1/2}$ | 0.288 | 0.208 | 0.200 | 0.21, 0.15 |
|  | $^2S_{1/2}-^2P_{3/2}$ | 0.647 | 0.490 | 0.493 | 0.52 |
| Tl$^{2+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.295 | 0.218 | 0.213 | 0.30 |
|  | $^2S_{1/2}-^2P_{3/2}$ | 0.703 | 0.540 | 0.545 | 0.76 |
| Pb$^{3+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.281 | 0.223 | 0.221 | 0.20, 0.23 |
|  | $^2S_{1/2}-^2P_{3/2}$ | 0.703 | 0.574 | 0.585 | 0.53, 0.69 |
| Bi$^{4+}$ | $^2S_{1/2}-^2P_{1/2}$ | 0.256 | 0.226 |  |  |
|  | $^2S_{1/2}-^2P_{3/2}$ | 0.676 | 0.601 |  |  |

[a]Reference [2].
[b]References for experimental data quoted in 2.

this time with the usual integer $2(2l+1)$ occupation of the outermost closed shell of the core (usual CIDF method with spectroscopic orbitals). The comparison of results of both types of computations is presented in Tables III–VI. As can be seen from these tables the introduction of noninteger occupation number of the outermost closed shell of the core greatly improves the accuracy of our prediction of both transition energies and oscillator strengths obtained with the same basis set. We can also observe that influence of noninteger occupation number of outermost core shell on both transition energies and oscillator strengths diminishes for the higher stages of ionizations along the silver isoelectronic sequence as the core-valence correlation subsides. Therefore, we may conclude that introduction of noninteger occupation of the outermost core shell in the process of generation of spin-orbitals used to construct the CI wave function greatly facilitates proper representation of core-valence electron correlation at the same, rather short, basis set.

Tables III–VI as well as Figs. 1 and 2 demonstrate comparison of present CIDF and CIDF($q$) result with our previous theoretical predictions where core-valence correlation was represented in semiclassical core-polarization picture CIDF+CP [2]. As can be seen from both tables and figures our present CIDF($q$) results obtained with noninteger outermost core shell occupation number are in a very good agreement with experimental data (for references to experimental data see [2]). Introduction of noninteger occupation number for the outermost core shell reduces the discrepancy between the usual CIDF results (with the same basis set) and experiment 50 times for $^2P_{1/2}$ and 10 times for $^2P_{3/2}$ levels, respectively, for the neutral end of isoelectronic sequence where core-valence electron correlation effect is most profound. Therefore, the method used in this study helps to properly include core-valence electron correlation within CI scheme at rather modest basis set not sufficient enough for the usual CI calculations. One should also note that very good agreement between present more accurate approach and our earlier DF+CP calculations [2] serves as another proof of applicability of our previous very simple DF+CP method where core-valence electron correlation was included through the core polarization model potential and appropriate corrections to the transition matrix element *within the single-configuration Dirac-Fock scheme*.

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