

Configuration interaction calculation of the specific mass shift for atoms with few valence electrons.

J. C. Berengut¹, V. V. Flambaum¹, and M. G. Kozlov^{2*}

¹ *University of the New South Wales, Sydney, Australia and*

² *Petersburg Nuclear Physics Institute, Gatchina, 188300, Russia*

(Dated: March 18, 2005)

We use valence configuration interaction method to calculate specific mass shift for several atoms and ions with few valence electrons.

Note: This is a work sheet and by no means a draft of the paper. I collected here as much information about the calculations as I could, so that we can cross check everything later if needed.

PACS numbers: 31.30.Jv, 06.20.Jr, 95.30.Dr

I. SMS OPERATOR.

We use relativistic atomic package based on the Dirac equation. However, we use non-relativistic approximation for the operator, which describes specific mass shift (SMS):

$$H_{\text{SMS}} = \frac{1}{M} \sum_{i>k} \vec{p}_i \cdot \vec{p}_k. \quad (1)$$

Because of the non-relativistic nature of this operator, we apply it only to the upper components of the Dirac wave functions.

The SMS operator H_{SMS} is added to the many-particle Hamiltonian:

$$H_\lambda = H_0 + \lambda H_{\text{SMS}}. \quad (2)$$

The eigenvalue problem for the Hamiltonian (2) is solved for $+\lambda$ and for $-\lambda$. Then, the SMS correction to the energy is recovered as:

$$\text{SMS} = \frac{E_{+\lambda} - E_{-\lambda}}{2\lambda}. \quad (3)$$

The Eq. (2) corresponds to the well known finite field method, which is very convenient for the scalar two-electron operators like (1) because

1. the symmetry and the structure of the operator (2) is the same as for initial Hamiltonian H_0 ;
2. only the eigenvalues of the Hamiltonian H_λ are necessary.

In this work we restrict ourselves to the frozen-core approximation. We first solve the Dirac-Fock equations for the core and valence electrons. Then we generate the basis set which in addition to the core and valence orbitals includes a number of virtual orbitals. Finally we do the configuration interaction (CI) calculation. If technically

possible, we allow all configurations for the valence electrons, but the core ones are frozen (full valence CI for a given basis set). For more complicated cases, when the size of the CI space becomes to large, we allow only for single and double excitations of the valence electrons (valence SD-CI).

The SMS operator for the valence electrons in the frozen core approximation can be divided into the core, one-electron, and two-electron parts:

$$H_{\text{SMS}} = H_{\text{SMS}}^{(0)} + H_{\text{SMS}}^{(1)} + H_{\text{SMS}}^{(2)} \quad (4)$$

The first term in (4) corresponds to the change of the core potential. It accounts for the change of the core orbitals when the Dirac-Fock equations are solved for the operator H_λ . The term $H_{\text{SMS}}^{(1)}$ accounts for the exchange interaction of the valence electrons with the core:

$$\langle i | H_{\text{SMS}}^{(1)} | k \rangle = - \sum_{j=1}^{N_{\text{core}}} \langle i, j | H_{\text{SMS}} | j, k \rangle. \quad (5)$$

The last term in (4) corresponds to the interaction between two valence electrons.

II. DETAILS OF THE CALCULATIONS

In this work we calculated SMS for the low-lying levels of the following atoms and ions: Mg I, Si II, Ti II, Cr II, Fe II, and Ni II. All of them have two, or more valence electrons. The atoms with one valence electron were calculated in [1], where the core-valence correlations were included. Si II, which has a ground state configuration $3s^2 3p$ was calculated in [1] as a one-electron ion, while here we treat it as a three-electron ion. Comparison of the two calculations allows to estimate the accuracy of the approximations used.

Many ions which we consider here were recently calculated in [2] in connection to the astrophysical search of the α -variation. For all these ions we use here the same configuration sets as were used there. We also tried to use as close basis sets as possible to those used in [2]. In some cases we were not able to reproduce the basis

*Electronic address: mgk@MF1309.spb.edu

sets exactly, which led to small differences in calculated spectra. These differences were always smaller than the differences between the theory and the experiment.

We used $\lambda = 0.005$ in Eq. (3) for all atoms. This value is small enough to neglect the higher orders, and large enough to give high numerical accuracy. The size of the nonlinear terms in λ were checked for Ti II, where we performed independent calculations for all three terms in (4) and additional calculation with the whole operator H_{SMS} (see Table VI). If nonlinear terms were important the sum of the three individual contributions would differ from the total SMS correction.

Mg I.

Mg I has configuration $[\text{Ne}]3s^2$. It is one of the simplest and well studied two-electron atoms. Because of that it is often used as a test ground for different methods of atomic calculations. Here we present results of the SMS calculations for 14 low-lying levels of Mg I. Three different calculations have been done:

1. The basic one-configurational calculation for the ground state $^1S_0[3s^2]$ and for the $^{1,3}P_J[3s3p]$ states. All core orbitals and orbitals $3s$ and $3p$ are formed in the V^{N-2} approximation (i.e. by solving Dirac-Fock equations for the Ne-like core).
2. Full two-electron CI for the medium size basis set $[8sp5d]$, which includes the orbitals $1-8s_{1/2}$, $2-8p_j$ and $3-5d_j$
3. Full two-electron CI for the basis set $[12spd9f]$. This basis set is formed by truncation of the basis set $[17spd12f]$ formed from the B -splines. This calculation is already very close to the saturation of the valence CI. Here the difference of the theoretical spectrum from the experiment is mostly caused by the neglect of the core-valence correlations.

TABLE I: Mg I. CI calculation of the 2-electron valence binding energies (in a.u.) and transition frequencies (in cm^{-1}).

| Level | E_{val} | ω_{theor} | ω_{exper} |
|-----------------|------------------|-------------------------|-------------------------|
| $^1S_0(3s^2)$ | 0.818049 | | |
| $^3S_1(3s4s)$ | 0.633904 | 40415.2 | 41197.403 |
| $^3S_0(3s4s)$ | 0.623499 | 42698.8 | 43503.333 |
| $^1D_2(3s3d)$ | 0.612428 | 45128.6 | 46403.065 |
| $^3D_1(3s3d)$ | 0.603947 | 46989.9 | 47957.058 |
| $^3D_2(3s3d)$ | 0.603947 | 46989.9 | 47957.027 |
| $^3D_3(3s3d)$ | 0.603947 | 46989.9 | 47957.045 |
| $^3P_0^o(3s3p)$ | 0.722782 | 20908.7 | 21850.405 |
| $^3P_1^o(3s3p)$ | 0.722690 | 20928.9 | 21870.464 |
| $^3P_2^o(3s3p)$ | 0.722504 | 20969.7 | 21911.178 |
| $^1P_1^o(3s3p)$ | 0.660897 | 34490.9 | 35051.264 |
| $^3P_0^o(3s4p)$ | 0.602641 | 47276.6 | 47841.119 |
| $^3P_1^o(3s4p)$ | 0.602626 | 47279.9 | 47844.414 |
| $^3P_2^o(3s4p)$ | 0.602595 | 47286.7 | 47851.162 |

TABLE II: Mg I. Calculations of the SMS (in $\text{GHz} \cdot \text{amu}$). For some levels we give medium (M) CI and one-configurational results in addition to the large (L) CI ones.

| Level | SMS | | | | CI |
|-----------------|------|------|------|----------|----|
| | (0) | (1) | (2) | Σ | |
| $^1S_0(3s^2)$ | -559 | 883 | -131 | 193 | L |
| " | -561 | 881 | -135 | 186 | M |
| " | -857 | 1125 | 0 | 268 | S |
| $^3S_1(3s4s)$ | -422 | 615 | -44 | 149 | L |
| " | -431 | 624 | -52 | 142 | M |
| $^3S_0(3s4s)$ | -415 | 615 | -21 | 179 | L |
| " | -424 | 630 | -30 | 177 | M |
| $^1D_2(3s3d)$ | -343 | 616 | 267 | 541 | L |
| $^3D_1(3s3d)$ | -375 | 561 | -41 | 144 | L |
| " | -381 | 571 | 10 | 200 | M |
| $^3D_2(3s3d)$ | -375 | 561 | -41 | 144 | L |
| $^3D_3(3s3d)$ | -375 | 561 | -41 | 144 | L |
| $^3P_0^o(3s3p)$ | -428 | 853 | 144 | 570 | L |
| $^3P_1^o(3s3p)$ | -428 | 852 | 145 | 569 | L |
| $^3P_2^o(3s3p)$ | -428 | 850 | 145 | 567 | L |
| " | -431 | 850 | 142 | 561 | M |
| " | -759 | 1161 | 266 | 668 | S |
| $^1P_1^o(3s3p)$ | -408 | 698 | -329 | -38 | L |
| " | -411 | 700 | -341 | -52 | M |
| " | -946 | 1163 | -265 | -49 | S |
| $^3P_0^o(3s4p)$ | -402 | 630 | -13 | 215 | L |
| $^3P_1^o(3s4p)$ | -402 | 629 | -13 | 215 | L |
| $^3P_2^o(3s4p)$ | -402 | 629 | -13 | 214 | L |

Table I presents results of the full CI calculation on the basis set $[12spd9f]$ of the binding energies and transition frequencies for 14 low-lying levels of Mg I. Table II gives SMS for the same levels in different approximations. Contributions of individual terms in Eq. (4) are given as well as their sum. SMS is calculated from Eq. (3) with $\lambda = 0.005$. Comparison of our results with the experiment is done in Table III, where the normal mass shift (NMS) is added to SMS. We assume that the field shift for Mg is negligible.

TABLE III: Mg I. Comparison with the experiment of the MS for several transitions (in $\text{GHz} \cdot \text{amu}$).

| Transition | λ (\AA) | NMS | SMS | MS | | Ref. |
|---|-------------------------------|-----|------|-------|---------|------|
| | | | | theor | exper | |
| $^3P_0^o(3s3p) \rightarrow ^3S_1(3s4s)$ | 5167 | 318 | -420 | -102 | -125(2) | [3] |
| $^3P_1^o(3s3p) \rightarrow ^3S_1(3s4s)$ | 5173 | 318 | -420 | -102 | -122(1) | [3] |
| $^3P_2^o(3s3p) \rightarrow ^3S_1(3s4s)$ | 5184 | 317 | -418 | -101 | -123(2) | [3] |
| $^1S_0(3s^2) \rightarrow ^1P_1^o(3s3p)$ | 2852 | 577 | -230 | 347 | 437(7) | [4] |
| " | " | " | " | " | 441(7) | [3] |
| " | " | " | " | " | 412(4) | [5] |
| " | " | " | " | " | 434(9) | [6] |
| $^3P_1^o(3s3p) \rightarrow ^3D_2(3s3d)$ | 3832 | 429 | -425 | 4 | 19(1) | [6] |
| $^1S_0(3s^2) \rightarrow ^3P_1^o(3s3p)$ | 4570 | 357 | 377 | 734 | 843(0) | [7] |
| " | " | " | " | 734 | 837(0) | [7] |

TABLE IV: Si II. Experimental frequencies (in cm^{-1}) and calculated mass shifts (in $\text{GHz} \cdot \text{amu}$) for transitions from the ground state ${}^2P_{1/2}^o$. Calculated frequencies are in perfect agreement with [2] and are not given here. Result of the calculation [1] is marked with the star.

| Level | Transition from ${}^2P_{1/2}^o$ | | | | | |
|-----------------|---------------------------------|------|----------|------|-------|------|
| | ${}^{2S+1}L_J$ | SMS | ω | NMS | SMS | MS |
| ${}^2P_{1/2}^o$ | | 2219 | | | | |
| ${}^2P_{3/2}^o$ | | 2204 | 287 | 5 | -15 | -10 |
| ${}^4P_{1/2}$ | | 3702 | 44080 | 725 | 1484 | 2209 |
| ${}^4P_{3/2}$ | | 3697 | 44191 | 727 | 1478 | 2205 |
| ${}^4P_{5/2}$ | | 3688 | 44364 | 730 | 1469 | 2199 |
| ${}^2D_{3/2}$ | | 3194 | 55304 | 909 | 975 | 1884 |
| ${}^2D_{5/2}$ | | 3191 | 55320 | 910 | 973 | 1883 |
| ${}^2S_{1/2}$ | | 719 | 65495 | 1077 | -1500 | -423 |
| ${}^2S_{1/2}^*$ | | " | " | " | -1257 | -180 |

TABLE V: Ti II. CI calculations of the 3-electron valence binding energies (in a.u.) and transition frequencies (in cm^{-1}). The energies and frequencies are calculated for $\alpha = \alpha_0$, $\alpha = \sqrt{9/8}\alpha_0$, and $\alpha = \sqrt{7/8}\alpha_0$, where α_0 is the laboratory value of the fine structure constant. That allows to find factors q (in cm^{-1}) in Eq. (6b).

| Level | E_{val} | ω_{theor} | ω_{exper} | q |
|------------------|------------------|-------------------------|-------------------------|------|
| ${}^4F_{3/2}$ | 3.129242 | 0.0 | 0.0 | 0 |
| ${}^4F_{5/2}$ | 3.128800 | 97.0 | 94.1 | 94 |
| ${}^4F_{7/2}$ | 3.128175 | 234.1 | 225.7 | 228 |
| ${}^4F_{9/2}$ | 3.127366 | 411.6 | 393.4 | 402 |
| ${}^4G_{5/2}^o$ | 3.001293 | 28081.6 | 29554.4 | 376 |
| ${}^4G_{7/2}^o$ | 3.000428 | 28271.4 | 29734.5 | 578 |
| ${}^4G_{9/2}^o$ | 2.999356 | 28506.7 | 29968.3 | 819 |
| ${}^4G_{11/2}^o$ | 2.998094 | 28783.7 | 30240.9 | 1095 |
| ${}^4F_{3/2}^o$ | 2.995337 | 29388.7 | 30836.3 | 527 |
| ${}^4F_{5/2}^o$ | 2.994789 | 29509.0 | 30958.5 | 659 |
| ${}^4F_{7/2}^o$ | 2.994064 | 29668.1 | 31113.7 | 822 |
| ${}^4F_{9/2}^o$ | 2.993159 | 29866.8 | 31301.0 | 1016 |

Si II.

Si II has configuration $[\text{Ne}]3s^23p$. In this calculation we follow [2], where the basis set $[8spd5f]$ was used. The core and the valence orbitals $3s$, $3p$, and $4s$ are formed in V^N -approximation, the orbital $3d$ corresponds to the V^{N-2} -approximation. $4f$ is formed from $3d$. The remaining virtual orbitals are formed from the previous orbital of the same symmetry (i.e. nlj from $(n-1)lj$). CI includes all single and double and partly triple excitations. The spectrum is in perfect agreement with the calculation [2]. In [1] the SMS for Si II was calculated in the one-electron model, while here we consider Si II as a three electron ion. Our results are given in Table IV.

Ti II.

Ti II has configuration $[\text{Ar}]3d^24s$. The results of the full CI for three valence electrons are presented in Tables V – VII. Table V gives the energies and transition frequencies. The full CI is made for the basis set $[8spd5f]$ (38 orbitals). The orbitals $1s$, $2s$, $2p$, $3s$, $3p$, and $3d$ are formed by solving Dirac-Fock equations for the configuration $[1s^2 \dots 3p^6]3d^2$. After that Dirac-Fock equations with the same Hamiltonian are solved for $4s$ and $4p$ orbitals (V^{N-1} approximation). Finally, the remaining virtual orbitals are constructed from the Dirac-Fock ones by multiplication by the simple radial function and orthogonalization.

TABLE VI: Ti II. Calculations of the SMS (in $\text{GHz} \cdot \text{amu}$).

| Level | SMS | | | |
|------------------|-------|-------|------|----------------|
| | (0) | (1) | (2) | Σ total |
| ${}^4F_{3/2}$ | -8168 | 22509 | -388 | 13953 13949 |
| ${}^4F_{5/2}$ | -8162 | 22496 | -388 | 13946 13941 |
| ${}^4F_{7/2}$ | -8153 | 22476 | -387 | 13936 13931 |
| ${}^4F_{9/2}$ | -8142 | 22450 | -387 | 13921 13917 |
| ${}^4G_{5/2}^o$ | -8002 | 22283 | -84 | 14197 14195 |
| ${}^4G_{7/2}^o$ | -7996 | 22263 | -82 | 14185 14183 |
| ${}^4G_{9/2}^o$ | -7989 | 22239 | -81 | 14169 14167 |
| ${}^4G_{11/2}^o$ | -7981 | 22211 | -81 | 14149 14148 |
| ${}^4F_{3/2}^o$ | -8058 | 22381 | -265 | 14058 14058 |
| ${}^4F_{5/2}^o$ | -8054 | 22369 | -263 | 14052 14050 |
| ${}^4F_{7/2}^o$ | -8047 | 22351 | -263 | 14041 14039 |
| ${}^4F_{9/2}^o$ | -8038 | 22329 | -266 | 14025 14026 |

TABLE VII: Ti II. SMS and normal mass shift (NMS) for several transitions (in $\text{GHz} \cdot \text{amu}$). Results of the calculations of the SMS in the one-configurational approximation are given for comparison and are marked with the star.

| Transition | ω cm^{-1} | NMS | SMS | | | | MS ¹ | |
|--|------------------------------|-----|-----|------|-----|----------|-----------------|-------|
| | | | (0) | (1) | (2) | Σ | theor | exper |
| ${}^4F_{3/2} \rightarrow {}^4G_{5/2}^o$ | 29554 | 486 | 166 | -226 | 304 | 244 | 730 | |
| | | | 386 | -453 | 139 | 72 | 558* | |
| | | | 449 | -462 | 16 | 3 | 510* | |
| $\rightarrow {}^4F_{3/2}^o$ | 30836 | 507 | 110 | -128 | 123 | 105 | 612 | |
| | | | 457 | -479 | 16 | -5 | 504* | |
| $\rightarrow {}^4F_{5/2}^o$ | 30959 | 509 | 114 | -140 | 125 | 99 | 608 | |
| | | | 387 | -470 | 139 | 56 | 547* | |
| ${}^4F_{9/2} \rightarrow {}^4G_{11/2}^o$ | 29848 | 491 | 161 | -239 | 306 | 228 | 719 | 487 |
| | | | 104 | -121 | 121 | 104 | 612 | 824 |
| $\rightarrow {}^4F_{9/2}^o$ | 30908 | 508 | 446 | -461 | 16 | 1 | 509* | |

¹Experimental data from Ref. [8].

Table VI also gives the values of the parameters q , which describe α -dependance of the transition frequencies (see [2] and Sec. III for details). For the even-parity states we give only levels of the ground multiplet 4F_J . Experiment shows that the second multiplet lies only 1000 cm^{-1} higher and belongs to the configuration $3d^3$. Valence CI places this multiplet much further up, at

about 4000 cm^{-1} . More realistic calculations for this multiplet should include core-valence correlations.

Calculations of the SMS in Tables VI and VII are made using Eq. (3) with $\lambda = 0.005$. In these tables we give contributions of different terms in Eq. (4) and their sum. In addition we independently calculate total SMS. This allows to check the linearity. It is seen that the sum of three contributions and the total SMS differs very slightly. So, we conclude that $\lambda = 0.005$ is sufficiently small. All calculations of SMS are done with this λ .

Results from the Table VI are used in Table VII to calculate SMS for several transitions. It may be interesting to see how much the answer depends on the correlations between the valence electrons. Table VII also gives SMS for the same transitions in one-configurational approximation. Note that not only the total SMS for each transition is very different, but also the contributions from the core, one-electron, and two-electron terms in Eq. (4). Comparison to the experiment in Table VII is done in the assumption of the absence of the volume shift. Note that in the paper [8] the claim is made that the volume shift has been seen for Ti [9].

Cr II.

Cr II has configuration $[\text{Ar}]3d^5$. For this calculation (see Table VIII) we use the same basis set $[6sp12d6f]$ and the same configurational sets as in [2]. The valence Dirac-Fock orbitals correspond to the following configurations: $3d$ for $3d^5$, $4s$ for $3d^44s$, and $4p$ for $3d^44p$. The virtual orbitals are formed from the valence orbitals as earlier. It is not possible here to make a full five-electron CI, so the sets of configurations for even-parity and odd-parity states include only SD excitations from the corresponding leading configurations.

TABLE VIII: Cr II. Calculated frequencies (in cm^{-1}) and mass shifts (in $\text{GHz}\cdot\text{amu}$) for transitions from the ground state ${}^6S_{5/2}$. Small differences in frequencies with the calculation [2] are probably due to the differences in the basis set, most likely in the method of the generation of the virtual states.

| Level ${}^{2S+1}L_J$ | Transition from ${}^6S_{5/2}$ | | | | | |
|-------------------------|-------------------------------|----------|-----|-------|-------|--|
| | SMS | ω | NMS | SMS | MS | |
| ${}^6S_{5/2}$ | 44824 | | | | | |
| ${}^6D_{5/2}$ | 41730 | 12989 | 214 | -3094 | -2880 | |
| ${}^6D_{7/2}$ | 41720 | 13175 | 217 | -3104 | -2888 | |
| ${}^6F_{1/2}^o$ | 42399 | 47004 | 773 | -2425 | -1652 | |
| ${}^6F_{3/2}^o$ | 42394 | 47092 | 774 | -2430 | -1656 | |
| ${}^6F_{5/2}^o$ | 42385 | 47239 | 777 | -2439 | -1662 | |
| ${}^6F_{7/2}^o$ | 42374 | 47443 | 780 | -2450 | -1670 | |
| ${}^6F_{9/2}^o$ | 42360 | 47702 | 784 | -2464 | -1680 | |
| ${}^6F_{11/2}^o$ | 42344 | 48015 | 790 | -2480 | -1691 | |
| ${}^6P_{3/2}^o$ | 42160 | 48547 | 798 | -2664 | -1866 | |
| ${}^6P_{5/2}^o$ | 42152 | 48673 | 800 | -2672 | -1871 | |
| ${}^6P_{7/2}^o$ | 42140 | 48861 | 803 | -2684 | -1881 | |

Fe II.

TABLE IX: Fe II. Calculated frequencies (in cm^{-1}) and mass shifts (in $\text{GHz}\cdot\text{amu}$) for transitions from the ground state ${}^6D_{9/2}$. Again there are some differences in frequencies with the calculation [2]. Results obtained without configuration $3d^54p$ are marked with the star and one-configurational results are marked with the dagger. MS_+ is obtained from calculations with $\lambda = +0.005$ and $\lambda = 0$.

| Level | Transition from ${}^6D_{9/2}$ | | | | | |
|------------------|-------------------------------|-------------------------------|--------|------|-------|---------------|
| | SMS | ω (cm^{-1}) | NMS | SMS | MS | MS_+ |
| | | theor. | exper. | | | |
| ${}^6D_{9/2}$ | 84429 | | | | | |
| " | 85727 | | | | | † |
| ${}^6D_{7/2}$ | 84410 | 372 | 385 | 6 | -19 | -13 |
| ${}^6D_{5/2}$ | 84396 | 650 | 668 | 11 | -33 | -22 |
| ${}^6D_{9/2}^o$ | 85579 | 38353 | 38459 | 632 | 1150 | 1782 |
| ${}^6D_{7/2}^o$ | 85570 | 38555 | 38660 | 636 | 1141 | 1777 |
| " | 87265 | | | 636 | 1538 | 2174 |
| ${}^6F_{11/2}^o$ | 85663 | 41864 | 41968 | 690 | 1234 | 1925 |
| ${}^6F_{9/2}^o$ | 85656 | 42012 | 42115 | 693 | 1227 | 1920 |
| ${}^6F_{7/2}^o$ | 85650 | 42141 | 42237 | 695 | 1221 | 1916 |
| " | 87305 | | | 695 | 1578 | 2273 |
| ${}^6P_{7/2}^o$ | 85485 | 42715 | 42658 | 701 | 1056 | 1757 |
| " | 87357 | | | 701 | 1630 | 2331 |
| ${}^8P_{7/2}^o$ | 81381 | 54914 | 54490 | 896 | -3048 | -2152 |
| " | 81381 | 54912 | | 896 | -3048 | -2152 |
| " | 81120 | | | 896 | -4607 | -3711 |
| ${}^6P_{7/2}^o$ | 81403 | 65171 | 62172 | 1022 | -3026 | -2003 |
| " | 81317 | | | 1022 | -4410 | -3388 |
| ${}^4F_{7/2}^o$ | | 65743 | 62066 | 1021 | | 1730 |
| " | 86902 | | | 1021 | 1175 | 2196 |

Fe II has configuration $[\text{Ar}]3d^64s$. Here again we follow the work [2]. We use the basis set $[6spdf]$ with the valence functions corresponding to the V^N approximation and CI includes all SD excitations. The spectrum for Fe II is very dense, and identification of some levels may be problematic [2]. Because of that we calculate g -factors to link together the levels calculated with $\lambda = 0, \pm 0.005$. Results are presented in Table IX.

In order to reach the level ${}^6P_{7/2}^o$ of the configuration $3d^54s4p$ we exclude configuration $3d^54p$ (we use Davidson algorithm for diagonalization which can not handle too many levels). Another level (${}^8P_{7/2}^o$) of the same configuration can be calculated both with and without configuration $3d^54p$ and result for the SMS does not change.

For the level ${}^4F_{7/2}^o$ of the configuration $3d^54p$ we could not reach convergence for $\lambda = -0.005$. Thus we calculated SMS using $\lambda = +0.005$ and $\lambda = 0$. The same was done for all other levels to see how this may change the answer. With except of two levels of the configuration $3d^54s4p$ there is no significant difference between these two calculations. It can be explained by the fact that total SMS for all these levels differ only by few percent. For the levels of the configuration $3d^54s4p$ the difference is three times bigger. Therefore, the non-linear terms in

λ may be more important.

In addition we make one-configurational calculation for several levels. It is seen that the role of correlations is less important here than in Mg I and Ti II. Because of that we can expect that, in spite of the high complexity of the spectrum, our results for Fe II are sufficiently reliable.

Ni II.

Ni II has configuration $[\text{Ar}]3d^9$. In this calculation we follow [2] and use the basis set $[5spdf]$. The core and the valence orbitals $3d$, $4s$, and $4p$ are formed in V^N -approximation. The orbitals $4d$, $4f$, $5s$, and $5p$ correspond to the V^{N-2} -approximation (configurations $3d^6 \dots$). The remaining virtual orbitals $5d$ and $5f$ are formed from the previous orbital of the same symmetry (nlj from $(n-1)lj$). The spectrum is in good agreement with the calculation [2].

TABLE X: Ni II. Experimental frequencies (in cm^{-1}) and calculated mass shifts (in $\text{GHz} \cdot \text{amu}$) for transitions from the ground state ${}^2D_{5/2}$. Calculated frequencies are in a close agreement with [2] and are not given here.

| Level | Transition from ${}^2D_{5/2}$ | | | | |
|-----------------|-------------------------------|----------|-----|-------|-------|
| | SMS | ω | NMS | SMS | MS |
| ${}^2D_{5/2}$ | 155999 | | | | |
| ${}^2D_{3/2}$ | 155925 | 1507 | 25 | -75 | -50 |
| ${}^4D_{7/2}^o$ | 152808 | 51558 | 848 | -3192 | -2344 |
| ${}^4D_{5/2}^o$ | 152742 | 52739 | 867 | -3257 | -2390 |
| ${}^4G_{7/2}^o$ | 152854 | 54263 | 892 | -3146 | -2254 |
| ${}^4G_{5/2}^o$ | 152795 | 55019 | 905 | -3204 | -2300 |
| ${}^4F_{7/2}^o$ | 152886 | 55418 | 911 | -3213 | -2302 |
| ${}^4F_{5/2}^o$ | 152755 | 56075 | 922 | -3245 | -2323 |
| ${}^2G_{7/2}^o$ | 152759 | 56372 | 927 | -3240 | -2313 |
| ${}^2F_{7/2}^o$ | 152761 | 57080 | 939 | -3239 | -2300 |
| ${}^2D_{5/2}^o$ | 152738 | 57420 | 944 | -3261 | -2317 |
| ${}^2F_{5/2}^o$ | 152705 | 58493 | 962 | -3295 | -2333 |

III. SUMMARY

Table XI summarise results of the MS calculations for the transitions used in astrophysical search for α -variation. This table also gives calculated values of the parameters q which define the α -dependence of the transition frequencies:

$$\omega_i = \omega_i^{(0)} + \omega_i^{(2)} \alpha^2 + \dots \quad (6a)$$

$$= \omega_{i,\text{lab}} + q_i x + \dots, \quad x \equiv (\alpha/\alpha_0)^2 - 1, \quad (6b)$$

where α_0 stands for the laboratory value of the fine structure constant. Note, that Eq. (6a) corresponds to the expansion at $\alpha = 0$, while Eq. (6b) — to the expansion at $\alpha = \alpha_0$. All coefficients q , with exception of Ti II transitions were calculated in [2].

TABLE XI: Final results for the MS for the transitions used in astrophysical search for α -variation. Parameters q from Eq. (6) are given for comparison [2]. Estimated errors are in brackets. MS for the ion Zn II was calculated in [1].

| Ion | Transition | ω_0 | q | MS |
|-------|---|------------------|------------------|-------------------------------|
| | | cm^{-1} | cm^{-1} | $\text{GHz} \cdot \text{amu}$ |
| Si II | ${}^2P_{1/2}^o \rightarrow {}^2D_{3/2}$ | 55309 | 520 (30) | 1900 (300) |
| | $\rightarrow {}^2S_{1/2}$ | 65500 | 50 (30) | -400 (500) |
| Ti II | ${}^4F_{3/2} \rightarrow {}^4F_{3/2}^o$ | 30836 | 530 (50) | 610 (30) |
| | $\rightarrow {}^4F_{5/2}^o$ | 30959 | 660 (70) | 610 (30) |
| Cr II | ${}^6S_{5/2} \rightarrow {}^6P_{3/2}^o$ | 48399 | -1360 (150) | -1900 (900) |
| | $\rightarrow {}^6P_{5/2}^o$ | 48491 | -1280 (150) | -1900 (900) |
| | $\rightarrow {}^6P_{7/2}^o$ | 48632 | -1110 (150) | -1900 (900) |
| Fe II | ${}^6D_{9/2} \rightarrow {}^6D_{9/2}^o$ | 38459 | 1330 (150) | 1800 (400) |
| | $\rightarrow {}^6D_{7/2}^o$ | 38660 | 1490 (150) | 1800 (400) |
| | $\rightarrow {}^6F_{11/2}^o$ | 41968 | 1460 (150) | 1900 (400) |
| | $\rightarrow {}^6F_{9/2}^o$ | 42115 | 1590 (150) | 1900 (400) |
| | $\rightarrow {}^6P_{7/2}^o$ | 42658 | 1210 (150) | 1800 (400) |
| | $\rightarrow {}^4F_{7/2}^o$ | 62066 | 1100 (300) | 1700 (400) |
| | $\rightarrow {}^6P_{7/2}^o$ | 62172 | -1300 (300) | -2000 (1000) |
| Ni II | ${}^2D_{5/2} \rightarrow {}^2F_{7/2}^o$ | 57080 | -700 (250) | -2300 (1000) |
| | $\rightarrow {}^2D_{5/2}^o$ | 57420 | -1400 (250) | -2300 (1000) |
| | $\rightarrow {}^2F_{5/2}^o$ | 58493 | -20 (250) | -2300 (1000) |
| Zn II | ${}^2S_{1/2} \rightarrow {}^2P_{1/2}^o$ | 48481 | 1584 (25) | 2110 (70) |
| | $\rightarrow {}^2P_{3/2}^o$ | 49355 | 2490 (25) | 2080 (70) |

In order to find coefficients q one calculates transition frequencies for several values of the parameter x . Here we use $x = 0$ and $x = \pm 1/8$. The former is used to calculate theoretical spectrum and SMS corrections, while coefficients q are found from the calculations with non-zero x : $q = 4(\omega_{x=1/8} - \omega_{x=-1/8})$.

As usual, it is difficult to estimate the accuracy of the SMS calculations presented here. We have seen that SMS correction consists of the three equally important contributions (Tables II and VI show that first two terms may be much larger, when the correction to the energy of a level is considered, but the third term becomes important for transition frequencies). We have also seen that correlations are also very important. Here we have accounted only for the valence-valence correlations. In the paper [1] it was shown that the core-valence correlations are also important (note the 20% difference between our result for Si II and that of the paper [1]). Of course, NMS is known precisely as long as the experimental transition frequency is known. Because of all that, we estimate the theoretical error bars for the MS to be 30% of the calculated SMS. For the ${}^6D_{9/2} \rightarrow {}^6P_{7/2}^o$ transition in Fe II the error bar is taken equal to the SMS because this transition is calculated in the one-configurational approximation. In Table XI the SMS values and the corresponding error bars for Zn II are taken from [1].

A. Correlations between SMS and q .

Table XI shows that there is strong correlation between SMS corrections and parameters q . That can lead to the systematic errors when astrophysical data are analyzed for the evidence of the *alpha*-variation at the cosmological time-scale. Indeed, because of this correlation, the evolution of the isotope abundances can mimic α -variation. Thus, it is important to analyze, whether it is possible to distinguish between these two effects. Table XI shows few examples where some combinations of the transition frequencies can be independent either on the nuclear mass, or on the value of α . As long as evolution of the isotope abundances for different elements can be independent, we can only make such combinations from the transitions of the same element.

For example, for Si II we can take the following combinations:

$$f_M = \omega_1 - 10\omega_2, \quad (7)$$

$$f_\alpha = \omega_1 + 4\omega_2, \quad (8)$$

where $\omega_{1,2}$ are the frequencies of the transitions ${}^2P_{1/2}^o \rightarrow$

${}^2D_{3/2}$ and ${}^2P_{1/2}^o \rightarrow {}^2S_{1/2}$.

The first combination practically does not depend on α , but is sensitive to the nuclear mass. The second, on the contrary, depends on α , but does not feel possible isotope evolution. Similar combinations exist for Ni II and Zn II, but not for Ti II, Cr II, or Fe II. With the help of the combinations of frequencies like (7) it is possible, at least in principle, to get experimental information about isotope evolution, which may be quite an interesting perspective for astrophysics. On the other hand, combinations of the type of (8) can give information about α -variation, which is free of the main source of systematics.

The obvious drawback of this scheme is the poor accuracy, with which we know SMS corrections. That makes it very important to improve the accuracy of the theory. It can be done by including the core-valence correlation corrections to the valence Hamiltonian by means of the many-body perturbation theory (MBPT) as it was done in [10]. The close analogy between the SMS operator (1) and the two-electron Coulomb interaction makes it relatively easy to include this interaction in MBPT part of the calculations as we did it here for the CI part.

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 [9] I (MK) have a problem with Ref. [8]. I have not read it carefully, so it is possible that I am simply missing something. It seems to me that there are some irregularities in splitting of the MS into NMS, SMS, and FS. I suggest we look at this paper once again more carefully.
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