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EVALUATION OF THE X-RAY TRANSITION ENERGIES FOR THE PAULI-PRINCIPLE-VIOLATING ATOMIC TRANSITIONS IN SEVERAL ELEMENTS BY USING THE DIRAC-FOCK METHOD

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Abstract

In the light of the ongoing upgrade of the VIP experiment and of other possible similar experiments, in this paper we analyze the Pauli-principle-violating atomic transitions of an electron for a wide class of metal conductors (Cu, Au, Ag, Ge, Pb). We remind that a Pauli-principle-violating atomic transition is defined as a radiative transition towards a final state that is already fully occupied. Of course, such transitions should not normally take place, because of the Pauli principle and these experiments are conceived in order to detect the possible tiny violations of the Pauli principle.

The aim of the present report is to provide the theoretical support to this class of experiments, by calculating the energy shifts that the emitted x-rays would undergo in the case of violation of the Pauli principle. We also provide an estimate for the relative transition rates, discuss the results and describe in some details the program used for the calculations.

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INTRODUCTION

The goal of the VIP experiment is to improve the limits on the probability of violation of the Pauli Exclusion Principle (PEP) through the search of "anomalous" X-ray in various atomic transitions. Such transitions should be produced by "fresh" electrons that are supposed to be introduced through an electrical current that cross the sample. The criterion of "freshness" is a very delicate one and will be dealt with in a separate publication; for what we are concerned here, we can just consider, on the basis of 'classical intuition', that these electrons are "new" with respect to the existing ones, in the sense that they come from the exterior of the sample. As such, they might be prone to a Pauli-forbidden transition with a higher probability (though extremely small!) than those already in the material, that were supposed to have had already the time to perform an eventual Pauli-forbidden transition [1] [2]. Such a probability is expressed through a parameter $\beta^2/2$ that depends on the conductivity of the material, according to the model proposed in [8].

In a previous report [3] we have calculated the energy-shift of emitted "Pauli-principle-violating" x-ray in the more plausible decay channels for copper atoms, with an uncertainty less than 10 eV. We had used a model where we supposed that the non-paulian electron capture in Cu atoms occurs as an usual radiative decay towards 1s states, though the latter was considered as doubly filled. This radiative decay could take place from 2p (K_α transition), 3p (K_β transition) or directly from valence states (K-edge emission). In these conditions, an energy shift with respect to the analogous 'non-Pauli-violating' (normal) radiative transitions is expected on the basis of the presence of an extra-electron in the final shell. As, in fact, the 1s shell is doubly filled already before the Pauli-violating transition, it provides a further screening of the ionic charge, thereby reducing the energy of the transition (ie, the transition energy shifts towards that of the Z-1 element, nickel in the case of copper). In these energy-shift calculations we had also supposed that the orbitals had no time to relax during the transition process (the so-called "sudden approximation"). As such transitions occur in a time of the order of $\Delta t \approx \hbar/\Delta E \approx 10^{-19}$ s (for $\Delta E \approx 8000$ eV), while the typical electron dynamics involves a much bigger time-scale, of the order 10^{-15} s, the sudden approximation is usually justified.

In the present work, we greatly improved the previous calculation by using the MDFGME program based on the Dirak-Fock metod. Such a program has the possibility to deal with non-antisymmetrized electrons, as shown by Mallow et al. [4] for a variety of muonic atoms, where

muons are considered as massive non-antisymmetrized electrons. In our case, the Pauli-violating electron was modeled as a particle with all the characteristics of a muon, but with the mass of the electron. Dirac-Fock approximation takes into account the relativistic corrections that are relevant for the heavy ions that we have considered for our samples (Z_{Cu} = 29, Z_{Ge} = 32, Z_{Ag} = 47, Z_{Au} = 79, Z_{Pb} = 82). The details of the calculations are illustrated below.

MOTIVATION

The VIP experiment aims at establishing new limits on the probability of the PEP violation. The best present result is $\beta^2/2 < 4.7 \times 10^{-29}$[6] [7], improving the previous Ramberg and Snow [8] limit by a factor of about 400. The new plans are to upgrade the VIP setup (VIP2) in order to be able to reach even more stringent limits. The experimental technique is to run a high electrical current through a Cu metal-conductor and to search for evidence of x rays emitted by a PEP-forbidden transition. Electrons passing through the conductor are assumed to have no previous contacts with it.

S.R.Elliot et al. [9] investigated the possibility to use Pb instead of Cu. There are two main reasons why Pb might help improving the measured limits on the PEP-forbidden transition. The first is that it produces higher-energy X-rays, which are less attenuated by absorption and therefore one can probe a larger number of transitions. The second is that it presents an increased separation between normal emission lines (K_α, K_b, etc.) and the equivalent PEP-forbidden transition, which allows a simpler analysis to identify an eventual PEP-forbidden transition. Apart from these two main reasons, it should be noted that in the model of [8] an increase in the resistivity leads to an increase of the $\beta^2/2$ parameter.

In this context we consider several metals that might be suitable for the future experiment, for which we calculate the PEP-violating transition energies.

CALCULATION METHOD AND USED PROGRAM

Thanks to the MCDFGME [10] numerical code it is possible to introduce a "multiconfiguration" approximation to the *N*-electron wave function and perform relativistic calculations to radiative transitions in atoms. This scheme proceeds through the optimization of the parameters during a self-consistent process [5]. Muons and electrons can be treated in analogous way through the self-consistent field theory, in order to obtain wave functions and energies. The

most commonly used approximation to treat the Hamiltonian of an *N*-electron system is the so called "no pair" approximation that explicity excludes electron-positron pairs. The effects of the Breit operator, the Lamb shift and all sort of radiative corrections are included. Therefore, the program [10] solves the multiconfiguration Dirac-Fock (MCDF) equations taking fully into account the relativistic effects. The underlying approach is based on both the central field approximation and a variational principle.

The Dirac-Fock method for obtaining an approximation to the wavefunction consists of three stages. In the first stage, a functional form for the wave function is selected and defined in terms of certain functions to be determined. This is the basis of the variational procedure and is usually done in terms of hydrogen-like wavefunctions that are combined in terms of some variational parameters (coefficients of linear combinations). Then an expression for the total energy is derived in terms of these functions and parameters. Finally, the variational principle is applied and equations are derived for the valid solutions that are the functions that leave the total energy stationary. The total wavefunction however must also satisfy certain criteria referred to as Hartree-Fock assumptions which are [11]:

1) The approximate total wavefunction is antisymmetric (of course, in our case, with the exception of the PEP violating one, which is not antisymmetrized).

2) The total wavefunction of N electrons atom, must consist of sums of products of N spin-orbitals of the form: $\varphi_{nlmlms}(r,\vartheta,\varphi)= (1/r)P(nl\ldots;r)Y_{lml}(\vartheta,\varphi)X_{ms}$;where $Y_{lml}(\vartheta,\varphi)$ is a spherical harmonic, X_{ms} is the spin function and $P(nl\ldots;r)$ is the radial function.

3) The one-particle wave-functions (spin-orbitals) should form an orthonormal set: $\int\varphi_{nlmlms}(1)\varphi_{n'l'ml'ms'}(1)d\tau_1= \delta_{nn'}\,\delta_{ll'}\,\delta_{ml\,ml'j}\,\delta_{ms\,ms'}$ where $d\tau_1$ represents integration over space and summation over the spin coordinates of electron 1.

4) The total wavefunction must be an eigenfunction of the total angular momentum operators L^2, L_z as well as the total spin operators S^2 and S_z.

Notice that the latter constraint is valid only at the atomic level and no more in a condensed-matter system. However, we did not modify it for our calculations.

The dependence of $P(nl\ldots;r)$ on the orbital quantum numbers varies from one type of single-configuration approximation (also called single-determinant) to another. In the MCDF approach, the approximation of the total wavefunction for the state is given by a linear combination of

configuration state functions of the form: $\Psi^{MCDF}(\gamma LS)=\Sigma_i c_i \varphi(\gamma_i LS)$ where $\varphi(\gamma_i LS)$ are the configuration state functions and c_i are the mixing coefficients satisfying the normalizing conditions: $\Sigma_i c_i^2=1$ and $<\varphi(\gamma_i LS)|\varphi(\gamma_j LS)>=\delta_{ij}$. In this approximation the energy is given by:
$E^{MCDF}=<\Psi^{MCDF}|H|\ \Psi^{MCDF}>=c^t(H_{ij})c$, *and:* $H_{ij}=<\varphi(\gamma_i LS)|H|\varphi(\gamma_j LS)>$.

In the calculations carried out here, we have taken into account the exact contribution of the Breit interaction. The magnetic part of the interaction was also included in the self-consistent process. The calculation was done with the keyword "electric" which computes the energy of two sets of configurations: initial and final, and then computes the electric transition rate between them. The magnetic transition rate between the two sets is not calculated because its probability is about four orders of magnitude less than the electric one. The overlap between the initial and final states is taken into account and the lack of orthogonally between the orbitals of the initial and final state is treated by the program so that all orbitals of each state are made self-consistent. The effect of orbital relaxation is also taken into account. Other minor effects, as the vacuum polarization or the one due to bound electrons, are included in the self-consistent process; also the Uehling potential is included in the Dirac-Equation. The Pauli violating electron (PVE) is treated by the program as a test particle of the same mass and spin as the electron, whose wavefunction is not antisymmetrized with the other electrons wavefunctions. As a result, extra configurations of the form *nlmnlm* concerning the PVE and other electrons are allowed. The exchange integrals between the PVE and other electronic states therefore vanish. We consequently assume that the PVE can move to any of the atomic shells during the transition. The input file of the program is given as the configurations in LS coupling and the program generates all the jj configurations arising from a given LS configuration and build the eigenstates of the total angular momentum. The average energy is computed for a total wavefunction of a linear combination of jj coupling multiconfigurations for a given J,M_j.

RESULTS AND DISCUSSION

In the following Tables, we list the results that we have obtained with MCDF for the PEP-violating transitions in several materials:

Transitions for Copper

Transition	Pauli obeying transitions	Pauli violating transitions		Energy difference
	Standard transition Energy [eV]	Energy [eV]	Transition probability velocity [1/s]	$E_{standard}$-E_{VIP} [eV]
$2p_{1/2}$ ==» $1s_{1/2}$ ($K_{\alpha 2}$)	8,047.78	7,728.92	2.6372675E+14	318.86
$2p_{3/2}$==» $1s_{1/2}$ ($K_{\alpha 1}$)	8,027.83	7,746.73	2.5690970E+14	279.84
$3p_{1/2}$ ==» $1s_{1/2}$ ($K_{\beta 2}$)	8,905.41	8,529.54	2.7657639E+13	375.87
$3p_{3/2}$==» $1s_{1/2}$ ($K_{\beta 1}$)	8,905.41	8,531.69	2.6737747E+13	373.72
$3d_{3/2}$==»$2p_{3/2}$ ($L_{\alpha 2}$)	929.70	822.84	5.9864102E+07	106.86
$3d_{5/2}$==»$2p_{3/2}$ ($L_{\alpha 1}$)	929.70	822.83	3.4922759E+08	106.87
$3d_{3/2}$==»$2p_{1/2}$ ($L_{\beta 1}$)	949.84	841.91	3.0154308E+08	107.93
$3s_{1/2}$ ==» $2p_{1/2}$	832.10	762.04	3.7036365E+11	70.06
$3s_{1/2}$ ==» $2p_{3/2}$	811.70	742.97	7.8424473E+11	68.73
$3d_{5/2}$ ==» 1s (**D**irect **R**adiative **R**ecombination)	8,977.14	8,570.82	1.2125697E+06	406.32

Transitions for Silver

Transition	Pauli obeying transitions [12]	Pauli violating transitions		Energy difference
	Standard transition Energy [eV]	Energy [eV]	Transition probability velocity [1/s]	$E_{standard}$-E_{VIP} [eV]
$2p_{1/2}$ ==» $1s_{1/2}$ ($K_{\alpha 2}$)	21,990.30	21,511.50	2.2470233E+15	478.80
$2p_{3/2}$==» $1s_{1/2}$ ($K_{\alpha 1}$)	22,162.92	21,680.22	2.1149182E+15	482.70
$3p_{1/2}$ ==» $1s_{1/2}$ ($K_{\beta 2}$)	24,911.54	24,294.44	3.4623828E+14	617.10
$3p_{3/2}$==» $1s_{1/2}$ ($K_{\beta 1}$)	24,942.42	24,322.91	3.3381051E+14	619.51
$3d_{3/2}$==»$2p_{3/2}$ ($L_{\alpha 2}$)	2,978.24	2,826.91	1.3521073E+13	151.33
$3d_{5/2}$==»$2p_{3/2}$ ($L_{\alpha 1}$)	2,984.34	2,832.43	7.9859607E+13	151.91
$3d_{3/2}$==»$2p_{1/2}$ ($L_{\beta 1}$)	3,150.97	2,995.63	7.0192256E+13	155.34
$3s_{1/2}$ ==» $2p_{1/2}$	2,806.11	2,679.09	4.4521991E+12	127.02
$3s_{1/2}$==» $2p_{3/2}$	2,633.66	2,503.79	1.0568161E+13	129.87
$4d_{5/2}$ ==» 1s (DRD)	25,145.50	24,795.70	1.1459870E+08	349.80

Transitions for Gold

Transition	Pauli obeying transitions	Pauli violating transitions		Energy difference
	Standard transition Energy [eV]	Energy [eV]	Transition probability velocity [1/s]	$E_{standard}$-E_{VIP} [eV]
$2p_{1/2}$ ==» $1s_{1/2}$ ($K_{\alpha 2}$)	66,990.73	66,207.58	2.1042335E+16	783.15
$2p_{3/2}$==» $1s_{1/2}$ ($K_{\alpha 1}$)	68,804.50	68,002.09	1.7835326E+16	802.41
$3p_{1/2}$ ==» $1s_{1/2}$ ($K_{\beta 2}$)	77,575.01	76,547.92	3.8657822E+15	1,027.09
$3p_{3/2}$==» $1s_{1/2}$ ($K_{\beta 1}$)	77,979.80	76,937.91	3.6994027E+15	1,041.89
$3d_{3/2}$==»$2p_{3/2}$ ($L_{\alpha 2}$)	9,628.05	9,374.76	1.9441580E+14	253.29
$3d_{5/2}$==»$2p_{3/2}$ ($L_{\alpha 1}$)	9,713.44	9,457.85	1.1406776E+15	255.59
$3d_{3/2}$==»$2p_{1/2}$ ($L_{\beta 1}$)	11,442.45	11,169.27	1.1012516E+15	273.18
$3s_{1/2}$ ==» $2p_{1/2}$	10,308.41	10,081.34	6.1287637E+13	227.07
$3s_{1/2}$==» $2p_{3/2}$	8,494.03	8,286.83	1.9449551E+14	207.20
$5d_{5/2}$ ==» 1s (DRD)	80,391.10	79,465.62	1.7569882E+09	925.48

Transitions for Germanium

Transition	Pauli obeying transitions	Pauli violating transitions		Energy difference
	Standard transition Energy [eV]	Energy [eV]	Transition probability velocity [1/s]	$E_{standard}$-E_{VIP} [eV]
$2p_{1/2}$ ==» $1s_{1/2}$ ($K_{\alpha 2}$)	9,855.42	9,526.21	4.1219591E+14	329.21
$2p_{3/2}$==» $1s_{1/2}$ ($K_{\alpha 1}$)	9,886.52	9,556.15	3.9968599E+14	330.37
$3p_{1/2}$ ==» $1s_{1/2}$ ($K_{\beta 2}$)	10,978.10	10,564.13	4.6200446E+13	413.97
$3p_{3/2}$==» $1s_{1/2}$ ($K_{\beta 1}$)	10,982.19	10,567.77	4.4603999E+13	414.42
$3d_{3/2}$==»$2p_{3/2}$ ($L_{\alpha 2}$)	1,188.01	1,086.91	6.2419796E+11	101.10
$3d_{5/2}$==»$2p_{3/2}$ ($L_{\alpha 1}$)	1,188.01	1,087.17	3.5828936E+12	100.84
$3d_{3/2}$==»$2p_{1/2}$ ($L_{\beta 1}$)	1,218.50	1,116.85	3.1603874E+12	101.65
$3s_{1/2}$ ==» $2p_{1/2}$	1,067.98	990.23	6.0350996E+11	77.75
$3s_{1/2}$==» $2p_{3/2}$	1,036.21	960.28	1.2977811E+12	75.93
$3d_{5/2}$ ==» 1s (DRD)	11,074.8	10,643.31	1.6890460E+10	431.49

Transitions for Lead

Transition	Pauli obeying transitions	Pauli violating transitions		Energy difference
	Standard transition Energy [eV]	Energy [eV]	Transition probability velocity [1/s]	$E_{standard}$-E_{VIP} [eV]
$2p_{1/2}$ ==» $1s_{1/2}$ ($K_{\alpha 2}$)	72,805.42	71,992.03	2.4680208E+16	813.39
$2p_{3/2}$==» $1s_{1/2}$ ($K_{\alpha 1}$)	74,970.11	74,133.89	2.0639102E+16	836.22
$3p_{1/2}$ ==» $1s_{1/2}$ ($K_{\beta 2}$)	84,450.45	83,385.36	4.5414771E+15	1,065.09
$3p_{3/2}$==» $1s_{1/2}$ ($K_{\beta 1}$)	84,939.08	83,856.44	4.3479248E+15	1,082.64
$3d_{3/2}$==»$2p_{3/2}$ ($L_{\alpha 2}$)	10,449.59	10,188.23	2.3146352E+14	261.36
$3d_{5/2}$==»$2p_{3/2}$ ($L_{\alpha 1}$)	10,551.60	10,287.71	1.3570636E+15	263.89
$3d_{3/2}$==»$2p_{1/2}$ ($L_{\beta 1}$)	12,613.80	12,330.02	1.3246599E+15	283.78
$3s_{1/2}$ ==» $2p_{1/2}$	11,349.40	11,116.39	7.4132768E+13	233.01
$3s_{1/2}$==» $2p_{3/2}$	9,184.56	8,974.38	2.4205005E+14	210.18
$5d_{5/2}$ ==» 1s(DRD)	87,589.00	86,686.79	5.8880291E+11	902.21

CONCLUSIONS

From the obtained results we can draw the following conclusions:

1) As the atomic number Z increases, the energy difference between the PEP violating and the standard transitions increases, as expected. This leads to a better separation and identification of the two emission lines. At the same time, also the probability of the transition increases with Z. This suggests that Au and Pb make good candidates, either for the future upgrade of the VIP experiment or for new experiments.

2) For all materials, the chains L_α (L_b) to K_α (K_β) have the highest transition probabilities compared to direct K-edge emission. Therefore, K_α and K_β lines are those that should be monitored in all cases.

From the technical point of view, we should notice the following:

1) We found that the Multiconfiguation Dirac-Fock (MCDF) was not very efficient for hole states calculations and so we preferred to use reference [12] for the standard transitions which uses relativistic many-body perturbation theory (RMBPT) to evaluate these quantities.

2) We had some difficulties to converge the calculations dealing with atoms with open outer shells (in particular, Ge and Pb). There are cases for which the average calculation did not converge. For this reason we have represented these configurations in terms of the approximate configurations with the nearest closed-shell configuration. The results of this approximation are very close to the open shell configuration for Group 11 and 6. A table comparison between the results, for the Ge, can be found in *Annex 1*.

Annex 1

AN EXAMPLE: **Exact Calculation**

Quantity	Result
Transition energy(eV)	9.5561134E+03
Transition wavelength (Ang)	1.2974332E+00
Transition Energy (cm-1)	7.7075257E+07
Transition Energy (MHz)	2.3106581E+12
Transition Energy (a.u.)	3.5118071E+02
Transition probability velocity (1/sec)	5.8498839E+13
Transition probability length (1/sec)	5.8358662E+13
Lifetime length gauge (sec)	1.7135417E-14
Lifetime velocity gauge (sec)	1.7094356E-14
Line strength Sobel'man's definition (a.u.)	1.8871872E-04
Oscillator strength (l)	8.8365835E-03
Oscillator strength (v)	8.8578089E-03

AN EXAMPLE: **Closed shell approximation**

Quantity	Result
Transition energy (eV)	9.5262075E+03
Transition wavelength (Ang)	1.3015063E+00
Transition Energy (cm-1)	7.6834050E+07
Transition Energy (MHz)	2.3034269E+12
Transition Energy (a.u.)	3.5008169E+02
Transition probability velocity (1/sec)	4.1219591E+14
Transition probability length (1/sec)	4.1118897E+14
Lifetime length gauge (sec)	2.4319719E-15
Lifetime velocity gauge (sec)	2.4260309E-15
Line strength Sobel'man's definition (a.u.)	8.9483637E-04
Oscillator strength (l)	1.0442194E-01
Oscillator strength (v)	1.0467766E-01

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