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Fine Structure Intervals $^2P^o_{3/2}$-$^2P^o_{1/2}$, $^2P_{3/2}$-$^2P_{1/2}$ and Electric Dipole Transition Rate $^2P_{3/2}$-$^2P^o_{1/2}$ in Phosphorus Isoelectronic Sequence $15 \le Z \le 50$ And Phosphorus Ions

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Abstract

A systematic study for the calculation of the fine structure intervals $^2P^o_{3/2}$-$^2P^o_{1/2}$ and $^2P_{3/2}$-$^2P_{1/2}$ for the ground configuration $3s^23p^3$ and the excited configuration $3s^23p^24s$ respectively, and electric dipole transition rate $^2P_{3/2}$-$^2P^o_{1/2}$ as well as transition energy form the excited configuration $3s^23p^24s$ to the ground configuration $3s^23p^3$ in Phosphorus isoelectronic sequence $15 \le Z \le 50$by applying multi-configuration Dirac-Fock (MCDF) method. The effect of Breit interaction, QED and correlation on the fine structure interval and the gauge invariance effect on the transition probability are studied. Also the fine structure intervals for the phosphorus ions from Piii to Pxv are calculated and are compared with the available experimental data and gives good consistent.

Keywords: ground configuration, excited configuration, multi-configuration Dirac-Fock, phosphorus ions

الخلاصة

دراسة منتظمة لحساب فترات التركيب الدقيق $^2P^o_{3/2}$ $^2P^o_{1/2}$ – و $^2P_{3/2}$ $^2P_{1/2}$ – للمستوى الارضي $3s^23p^3$ والمستوى المتهيج $3s^23p^24s$ على التوالي واحتمالية الانتقال لثنائي القطب الكهربائي $^2P_{3/2}$ $^2P^o_{1/2}$ –وكذلك طاقة الانتقال من المستوى المتهيج $3s^23p^24s$ الى المستوى الارضي $3s^23p^3$ للمتتابعة الالكترونية لذرة الفسفور $15 \le Z \le 50$ قد تم حسابهما باستخدام طريقة ديراك–فوك المتعددة التركيب الالكتروني. تم دراسة تأثير تفاعل بريت و تصحيح ديناميكية الالكترون الكمية وتاثير العلاقه المتبادله على فترة التركيب الدقيق ودراسة تاثير مقياس عدم التغير على احتمالية الانتقال. كذلك تم حساب فترات التركيب الدقيق لايونات الفسفور من Piii الى Pxv ومقارنتها بالنتائج العملية المتوفره حيث كان التوافق جيدا.

الكلمات المفتاحية: للمستوى الارضي، والمستوى المتهيج ، ديراك–فوك المتعددة التركيب الالكتروني، ايونات الفسفور.

1- Introduction

The study of atomic properties can be done by many tools, one of the best is the multiconfiguration Dirac-Fock method. Fine structure intervals are of relativistic origin and are very sensitive to relativistic, correlations, and quantum electrodynamics (QED) effects. Therefore correlated relativistic atomic calculations are required in order to produce accurate fine structure data for atoms or ions. Relativistic effects are included through using of Dirac's equation which includes relativistic corrections for a single-particle (Schiff, 1968). Correlation effect arises from the fact that the Dirac-Fock method which is the relativistic version of the Hartree-Fock method is an independent particle approximation. The correlation effect can be achieved by using multiconfiguration instead of single configuration. Relativistic correction to the Coulomb interaction between electrons is achieved through using of Breit interaction as a perturbation. Calculations of electric radiative transition rate have either been based on the Coulomb gauge or Babushkin gauge. The nonrelativistic limit of the former is the velocity form whereas the latter is the length form (Grant, 1970)

In the preceding paper (Hussain 2010), contributions of Breit interaction (magnetic and retardation contributions) and radiative QED effect (self-energy and vacuum polarization contributions) are studied and compared along the carbon isoelectronic sequence $6 \le Z \le 104$.

In this work we used the multiconfiguration Dirac-Fock method to calculate the fine structure intervals ${}^2P^o_{3/2}$-${}^2P^o_{1/2}$ and ${}^2P_{3/2}$-${}^2P_{1/2}$ of the ground configuration $3s^23p^3$ and the excited configuration $3s^23p^24s$ respectively. Also the paper includes the calculation of the allowed electric dipole transition between $3s^23p^23d$ ${}^2P_{3/2}$ excited state and $3s^23p^3$ ${}^2P^o_{1/2}$ ground state for phosphorus isoelectronic sequence. Our task in this paper is study the effect of Breit interaction, QED and correlation effect on the fine structure interval and the effect of gauge invariance on the electric dipole transition.

2- Theory

The starting point of the multi-configuration Dirac-Fock MCDF method is based on Dirac-Coulomb Hamiltonian (Grant 1970)

$$H_{DC} = \sum_{i=1}^{N} h_D(\vec{r}_i) + \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}\frac{1}{r_{ij}} \qquad (1)$$

where $h_D(\vec{r})$ is the one body Dirac Hamiltonian for an electron moving in nuclear potential V_{nuc} (Desclaux 1965)

$$h_D(\vec{r}) = c\vec{\alpha}\cdot\vec{p} + (\beta - 1)c^2 - V_{nuc} \qquad (2)$$

The atomic wavefunction $\Psi_\Gamma(JM)$ is composed of configuration state functions CSF $\Theta(\gamma\, JM)$ (Grant, McKenzeie, Norrington, Mayers and Pyper 1980), which are eigenfunction of the total angular momentum operators J^2 and J_Z.

$$\Psi_\Gamma(JM) = \sum_{r}^{n_c} c_r\, \Theta\ (\gamma_r\ JM) \qquad (3)$$

Where n_c denotes the number of CSF, c_r is the expansion coefficient and γ represent the configuration and any other quantum number required to specify the state.

The configuration state function $\Theta(\gamma\, JM)$ built from single electron orbital (Grant 2007)

$$\phi_{n\kappa m}(\vec{r}) = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\,\Omega_{\kappa m}(\theta,\varphi) \\ iQ_{n\kappa}(r)\,\Omega_{-\kappa m}(\theta,\varphi) \end{pmatrix} \qquad (4)$$

Where n is the principal quantum number, and κ is the relativistic angular quantum number. $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the one-electron radial wavefunctions respectively, and where $\Omega_{\kappa m}(\theta,\varphi)$ is the spherical spinor (Grant 1970).

In the multiconfiguration Dirac-Fock method, self-consistent field procedure both the radial functions and the expansion coefficients are optimized to self-consistency.

The former leads to a system of coupled differential equations, and the latter to a matrix eigenvalue problem. Once radial functions have been determined, relativistic configuration interaction calculation can be performed that include other effects. One of the most important is the Breit interaction operator (Breit 1929 1930, 1932)

$$B_0(i,j) = -\frac{1}{2}\left[\frac{\vec{\alpha}(i)\cdot\vec{\alpha}(j)}{r_{ij}} + \left(\vec{\alpha}(i)\cdot\vec{\nabla}(i)\right)\left(\vec{\alpha}(j)\cdot\vec{\nabla}(j)\right)r_{ij}\right] \tag{5}$$

The first term is called the magnetic (Gaunt) term and the second term is called the retardation term.

QED treatment introduces a correction to the electron-nucleus interaction called radiative QED correction. The main radiative QED contributions in electronic atom are electron self-energy and vacuum polarization corrections. The Self-Energy correction which is the most significant part of the radiative corrections arises from the interaction of the bound electron with its own radiation field (Dyall, Grant, Johnson, Parpia and Plummer 1989)

For one-electron systems, the lowest order self-energy has been calculated by P.J. Mohr (Mohr 1982, 1992) and expressed as:

$$E_{n\kappa}^{SE} = \left(\frac{\alpha}{\pi}\right)\frac{(Z\alpha)^4}{n^3}F_{n\kappa}(Z\alpha) \tag{6}$$

Where $F(Z\alpha)$ dimensionless power series function slowly varying of $Z\alpha$, its numerical values are employed from reference (Mohr and Taylor 2000)

For many electron atoms, an approximation was made to scale the above hydrogenic result, by replacing the atomic number Z by an effective atomic number Z^* defined as

$$Z^* = \frac{\langle r_{n\kappa}\rangle_H}{\langle r_{n\kappa}\rangle_{MCDF}} Z \tag{7}$$

Here $\langle r_{n\kappa}\rangle_H$ is the expectation value of the radius of the $n\kappa$ orbital in a hydrogen-like ion of atomic number *Z*, and $\langle r_{n\kappa}\rangle_{MCDF}$ is the radius of that orbital computed in the present MCDF calculation.

The self-energy is obtained by setting

$$H^{SE} = \sum_{a=1}^{n_w} q_r(a)\, E_{n_a\kappa_a}^{SE} \tag{8}$$

Where $q(a)$ is the occupation number of the orbital a, and n_w is the number of orbitals.

The second correction is Vacuum Polarization, which arises from the interaction of the bound electron with the virtual electron-positron pairs created in the field of the nucleus (K. J. Dyall 1989). The lowest order term of this correction is of order α with respect to the nuclear Coulomb potential can be evaluated, following Wichmann and Kroll (Wichmann and Kroll 1956), as the expectation value of the Uehling potential

$$H^{VP} = \sum_{a=1}^{n_w} q_r(a) \int_0^{\infty} dr U(r) \left[P^2_{n_a \kappa_a}(r) + Q^2_{n_a \kappa_a}(r) \right] \quad (9)$$

Where $U(r)$ is the Uehling potential (Uehling 1935)

Electric dipole transition probability A_{ij} from one level J_i to another level J_f is (Grant 1974)

$$A_{ij} = [J_i]^{-1} \sum_{M_i} \sum_{M_j} 2\pi \left| \langle \Psi_{\Gamma_i}(J_i) \| E1 \| \Psi_{\Gamma_j}(J_j) \rangle \right|^2 \quad (10)$$

Where $E1$ electric dipole operator.

3- Results And Discussions

A program acronym GRASP (General Relativistic Atomic Structure Package) developed by I.P. Grant and coworkers (Parpia, Fischer and Grant 1996) based on multiconfiguration Dirac-Fock method was used to done the calculations. The calculations of fine structure were divided in to two parts. The first one is applied on phosphorus isoelectronic in the atomic range $15 \le Z \le 50$ where the experimental data are not available. The second part is applied on the phosphorus ions in the range P iii to P vx where the experimental data are available. The ground configuration $3s^2 3p^3$ of the phosphorus consists of 5 levels all of odd parity, the states ${}^2P^o_{1/2}$ and ${}^2P^o_{3/2}$ are chosen to study the fine structure interval ${}^2P^o_{1/2}$ - ${}^2P^o_{3/2}$. The excited configuration $3s^2 3p^2 4s$ consist of 8 levels all of even parity, the states ${}^2P_{1/2}$ and ${}^2P_{3/2}$ are chosen to study the fine structure interval ${}^2P_{3/2}$ - ${}^2P_{1/2}$.

Table 1 lists the contributions of the calculated values of the fine structure interval ${}^2P^o_{3/2}$ - ${}^2P^o_{1/2}$ of the first order, Breit interaction and QED corresponding to the ground configuration $3s^2\ 3p^3$. The three contributions of the fine structure intervals shows rapid increasing with the nuclear charge where the Breit interaction contribution varies between 4.6% to 1.4% while the QED contribution varies between 0.03% to 0.16% of the total value of the fine structure intervals along the isoelectronic sequence.

In order to probe the influence of correlation on the fine structure intervals, table 2 reports the varies contributions to the fine structure interval ${}^2P^o_{3/2}$ - ${}^2P^o_{1/2}$ by adding the configuration *3p*^{2} *3d* to the original one *3s*^{2} *3p*^{3}. It is clear that the zero order contribution reduce by about 16.3% to 0.02%, the absolute value of the Breit interaction contribution reduce from 1.5% to 36% while the QED contribution increase from 14% to 1% from the values corresponding to table 1 along the isoelectronic sequence

Table 3 reports varies contribution to the fine structure interval $^2P_{3/2}$-$^2P_{1/2}$, these contributions shows increasing with the nuclear charge. Fine structure interval $^2P_{3/2}$-$^2P_{1/2}$ shows linear increasing with nuclear charge whiles the fine structure interval $^2P^o_{3/2}$-$^2P^o_{1/2}$ shows exponential increasing with nuclear charge as shown in fig 1 along the isoelectronic sequence $15 \leq Z \leq 50$.

In order to check the reality of our calculations, the calculated values of the fine structure intervals are compared with the experimental data. Table 4 shows varies contribution of the fine structure $^2P^o_{3/2}$-$^2P^o_{1/2}$ for the phosphorus ions P iii – P xv compared with the available experimental data. Generally the calculated values are in good agreement with the experiment except at some ions, also the contributions values of zero order, Breit interaction and QED) shows rapid decreasing with the increasing of the order of the principal quantum number.

In table 5 we present our theoretical transition energy as well as the electric dipole transition probability for the allowed transition $^2P_{3/2}$-$^2P^o_{1/2}$ where the transition probability are given in Babushkin and Coulomb gauges along the isoelectronic sequence $15 \leq Z \leq 50$.

Table 1: Fine structure interval ${}^2P^o_{3/2}$ - ${}^2P^o_{1/2}$ in cm^{-1} corresponding to the configuration $3s^2 3p^3$

Z	*Zero order*	*Breit*	*QED*	*Tot*
15	32.5768	-1.4513	0.01134	31.1321
16	56.1797	-3.478	0.04021	52.7388
17	102.7696	-7.15	0.1085	95.7278
18	185.7884	-13.26	0.247	172.7781
19	325.0019	-22.82	0.506	302.6898
20	547.314	-37.06	0.95	511.2163
21	887.6963	-57.36	1.66	832.0343
22	1389.7676	-85.11	2.747	1307.4012
23	2105.801	-122.23	4.33	1988.2664
24	3096.0554	-168.56	6.53	2933.7144
25	4427.508	-227	9.49	4209.7868
26	6172.2323	-298	13.33	5887.8983
27	8405.7735	-381	18.18	8043.1905
28	11205.8368	-476.7	24.05	10753.1513
29	14651.477	-586	31.2	14096.711
30	18822.793	-708	39.6	18153.862
31	23801.022	-843	49.6	23005.691
32	29668.889	-996	60.9	28734.693
33	36511.046	-1164	74.2	35425.209
34	44414.525	-1337	88.6	43163.879
35	53469.149	-1535	105.2	52040.066
36	63767.885	-1747	123.2	62146.217
37	75407.139	-1980	144	73578.169
38	88487.012	-2220	167	86435.411
39	103111.517	-2480	192	100821.308
40	119388.793	-2760	220	116843.311
41	137431.287	-3070	250	134613.149
42	157355.956	-3390	283	154247.023
43	179284.449	-3740	318	175865.789
44	203343.306	-4100	357	199595.16
45	229664.163	-4490	398	225565.9
46	258383.946	-4910	444	253914.025
47	289645.095	-5360	492	284781.022
48	323595.784	-5800	545	318314.061
49	360390.143	-6350	598	354666.227
50	400188.509	-6890	658	393996.756

Table 2: Fine structure interval ${}^{2}P^{o}_{3/2}$ - ${}^{2}P^{o}_{1/2}$ in cm^{-1} corresponding to $3s^2\ 3p^3+3p^2\ 3d$

Z	*Zero order*	*Breit*	*QED*	*Tot*
15	27.1518	-1.546	0.01319	25.6238
16	52.3586	-3.593	0.0429	48.807
17	99.4972	-7.27	0.1116	92.3333
18	182.7753	-13.39	0.2519	169.6323
19	322.2898	-22.96	0.511	299.8361
20	545.0866	-37.25	0.949	508.841
21	886.2357	-57.5	1.669	830.4242
22	1389.4364	-85.3	2.747	1306.9263
23	2107.0226	-122.17	4.32	1989.3617
24	3099.2894	-169.44	6.52	2936.856
25	4433.2184	-226.8	9.49	4215.4603
26	6180.857	-297.8	13.24	5896.5676
27	8417.6981	-380.7	18.1	8055.2689
28	11221.3782	-476.3	23.98	10768.9837
29	14670.878	-585	31.1	14116.568
30	18846.224	-708	39.5	18177.939
31	23828.595	-843	49.3	23034.119
32	29700.665	-995	60.6	28767.553
33	36547.048	-1154	73.3	35462.537
34	44454.744	-1337	87.7	43205.683
35	53513.562	-1534	104.5	52086.333
36	63816.449	-1747	123.5	62196.918
37	75459.808	-1970	144	73633.266
38	88543.73	-2220	166	86494.858
39	103172.226	-2480	191	100885.059
40	119453.434	-2760	219	116911.316
41	137499.799	-3060	248	134685.359
42	157428.279	-3390	282	154323.386
43	179360.522	-3730	317	175946.258
44	203423.073	-4100	356	199679.688
45	229747.564	-4490	397	225654.44
46	258470.926	-4910	442	254006.536
47	289735.6	-5350	491	284877.46
48	323689.759	-5800	547	318414.389
49	360487.538	-6360	600	354770.409
50	400289.272	-6790	660	394104.755

Table 3: Fine structure intervals in cm^{-1} of the $^{2}P_{3/2}$ - $^{2}P_{1/2}$ corresponding to the configuration 3p^2 4s

Z	*Zero order*	*Breit*	*QED*	*Tot*	*Exp*
15	330.4227	-16.53	0.1868	314.03769	297.792
16	577.58389	-27.42	0.3899	550.54209	523.97
17	919.98145	-41.36	0.704	879.30532	
18	1373.56669	-58.5	1.154	1316.24917	
19	1953.86031	-78.3	1.757	1876.98435	
20	2674.5675	-101.6	2.521	2575.4953	
21	3546.0382	-126.4	3.43	3422.6477	
22	4573.6015	-153.5	4.49	4424.5441	
23	5756.0255	-180.7	5.62	5580.9514	
24	7084.5	-207	6.82	6884.1819	
25	8542.5991	-232	7.85	8318.8784	
26	10107.5237	-254	8.9	9863.0453	
27	11752.534	-272	9.6	11490.3058	
28	13450.0058	-288	10.2	13172.8951	
29	15174.3012	-300	10.4	14884.6022	
30	16903.7811	-311	10.6	16602.9446	
31	18621.7194	-322	10.4	18310.2648	
32	20316.2782	-328	10.2	19993.8441	
33	21979.894	-346	9.9	21645.37	
34	23608.418	-360	9.5	23260.1024	
35	25200.2419	-370	9.3	24835.9926	
36	26755.5317	-390	8	26372.8939	
37	28275.6148	-410	8	27871.9208	
38	29762.518	-430	7	29334.959	
39	31218.637	-460	7	30764.312	
40	32646.506	-490	7	32162.462	
41	34048.659	-530	6	33531.9	
42	35428.147	-560	6	34871.896	
43	36786.02	-610	5	36191.157	
44	38124.972	-650	5	37488.433	
45	39446.91	-680	5	38765.612	
46	40753.551	-740	4	40024.388	
47	42046.432	-790	4	41266.275	
48	43326.921	-840	4	42492.613	
49	44596.234	-900	4	43704.585	
50	45855.442	-960	4	44903.229	

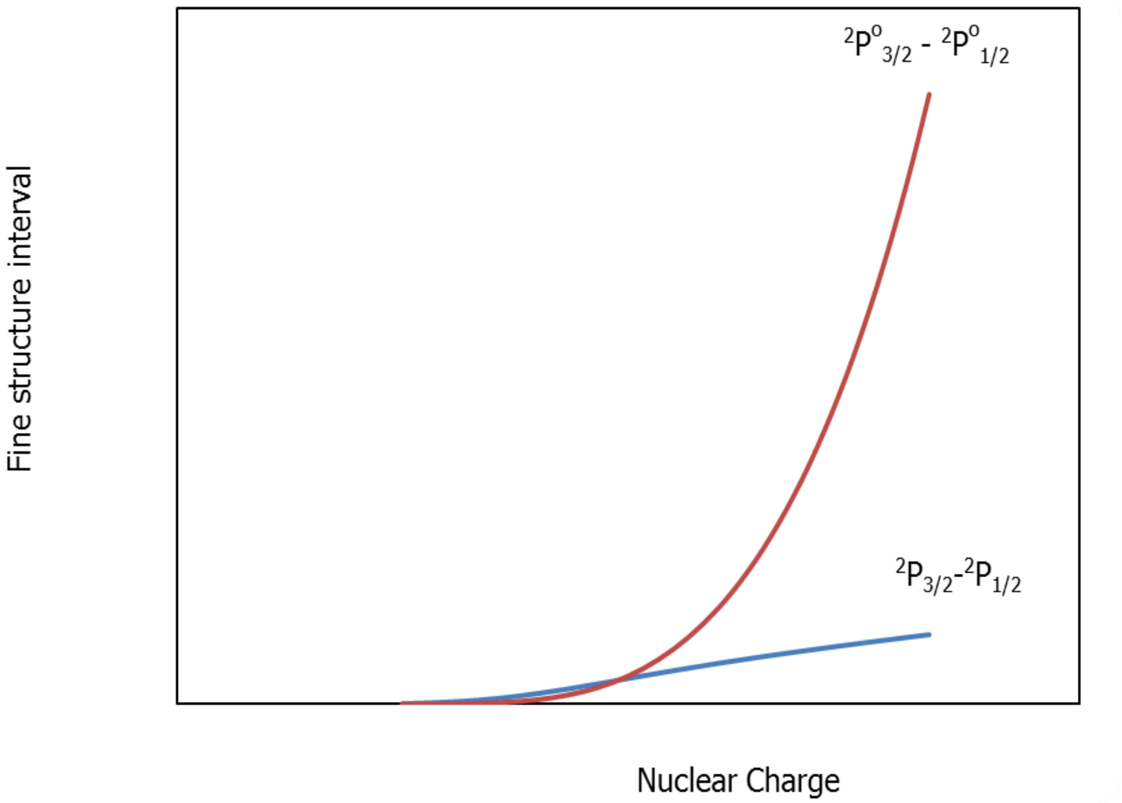

Fig.1: Fine structure intervals ${}^2P^o_{3/2}$ - ${}^2P^o_{1/2}$ and ${}^2P_{3/2}$ - ${}^2P_{1/2}$ as a function of nuclear charge in phosphorus isoelectronic sequence.

Table 4: Fine structure interval ${}^2P^o_{3/2}$ - ${}^2P^o_{1/2}$ in cm^{-1}

configuration	***Zero order***	***Breit***	***QED***	***Tot***	***Exp***
P iii $3s^2 3p$	593.26245	-27.4	0.397	566.22799	559.14
P iii $3s^2 4p$	136.916189	-6.11	0.0574	130.86512	136.72
P iii $3s^2 5p$	59.2702193	-2.64	0.0189	56.646114	117.35
P iii $3s^2 6p$	31.0782262	-1.39	0.00837	29.700386	17.48
P iii $3s^2 7p$	18.3124287	-81.7	0.0044	17.499874	
P iii $3s^2 8p$	11.6909945	-0.522	0.00259	11.1719	
P iii $3s^2 9p$	7.9162917	-0.353	0.00165	7.564791	
P v $2p^6 3p$	813.573638	-37.2	0.65	777.01134	795.38
P v $2p^6 4p$	292.818979	-13.5	0.179	279.47844	284.41
P v $2p^6 5p$	138.22688	-6.42	0.0734	131.87570	133.84
P v $2p^6 6p$	76.0388095	-3.55	0.037	72.528807	73.48
P v $2p^6 7p$	46.2408885	-2.16	0.0212	44.100562	44.7
P v $2p^6 8p$	30.1955377	-1.41	0.0133	28.795554	29.5
P v $2p^6 9p$	20.798112	-0.974	0.00884	19.832869	20.1

P vii 2s^2 2p^5	7584.60024	-365	11.7	7231.3825	7273
P xiii 1s^2 2p	11930.2142	-779	25.5	11176.79	11226
P xiii 1s^2 3p	3518.63288	-226	7.30	3300	3330
P xiii 1s^2 4p	1480.34068	-94.1	3.04	1389.2940	1530
P xv 2p	18628.966	0.0	41.4	18670.378	18670.3
P xv 3p	5521.06672	0.0	12.3	5533.3426	5533
P xv 4p	2328.61773	0.0	5.18	2333.7974	2333
P xv 5p	1191.93549	0.0	2.65	1194.5877	

Table 5: Transition energy (cm^{-1}) and electric dipole transition rate (sec^{-1}) from 3p^2 4s $^2P_{3/2}$ state to *3s^2 3p^3* $^2P_{1/2}$ *state*

Z	*Energy*	*A(Bab)*	*A(Coul)*
15	3.0977E+04	5.9725E+06	2.090375E+7
16	8.1160E+04	6.8483E+07	1.232694E+8
17	1.4244E+05	2.4872E+08	3.73080E+8
18	2.1487E+05	6.1559E+08	8.00267E+8
19	2.9835E+05	1.2581E+09	1.63553E+9
20	3.9279E+05	2.2938E+09	2.75256E+9
21	4.9812E+05	3.8763E+09	4.65156E+9
22	6.1428E+05	6.2031E+09	6.82341E+9
23	7.4121E+05	9.5180E+09	1.04698E+10
24	8.7887E+05	1.4108E+10	1.55188E+10
25	1.0272E+06	2.0288E+10	2.23168E+10
26	1.1862E+06	2.8384E+10	3.12224E+10
27	1.3557E+06	3.8704E+10	4.25744E+10
28	1.3557E+06	3.8704E+10	4.25744E+10
29	1.7263E+06	6.7115E+10	7.38265E+10
30	1.9272E+06	8.5696E+10	9.42656E+10
31	2.1386E+06	1.0751E+11	1.18261E+11
32	2.3603E+06	1.3282E+11	1.46102E+11
33	2.5924E+06	1.6190E+11	1.7809E+11
34	2.8348E+06	1.9509E+11	2.14599E+11
35	3.0876E+06	2.3273E+11	2.3273E+11
36	3.3243E+06	2.8230E+11	2.8230E+11
37	3.6238E+06	3.2301E+11	3.2301E+11

38	3.9072E+06	3.7654E+11	3.7654E+11
39	4.2009E+06	4.3632E+11	4.3632E+11
40	4.6542E+06	8.7190E+09	8.45743E+9
41	4.9873E+06	8.3181E+09	8.068557E+9
42	5.3325E+06	7.9455E+09	7.62768E+9
43	5.6897E+06	7.6000E+09	7.296E+9
44	6.0591E+06	7.2799E+09	6.988704E+9
45	6.4408E+06	6.9835E+09	6.634325E+9
46	6.8349E+06	6.7089E+09	6.373455E+9
47	7.2414E+06	6.4544E+09	6.067136E+9
48	7.6605E+06	6.2183E+09	5.845202E+9
49	8.0922E+06	5.9992E+09	5.579256E+9
50	8.5368E+06	5.7956E+09	5.389908E+9

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