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Has a possible change of the values of the physical constants a role in biological evolution?

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Abstract. In the light of renewed discussions about variations in the fundamental constants we have investigated the effect of changing the fine-structure constant α on the chemistry of medium and heavy elements important for metal-containing biological molecules. Relativistic Hartree-Fock calculations performed for Fe^{2+} and Fe^{3+} ions (important, e.g., for haemoglobin) indicate that a five-times larger α can change energy levels and valence directionality significantly. Other relativistic effects in chemistry are discussed.

1. Introduction

Dirac's large-number hypothesis [1] stipulates that large fundamental dimensionless 'constants' such as the ratio of the electric to the gravitational force between proton and electron ($e^2/Gm_p m_e$) $\approx 7 \times 10^{39}$ are in fact varying, i.e. increasing with the age of the universe. In particular, Dirac postulated that the gravitational constant G decreases linearly in time t so that the above ratio is proportional to the age of the universe. If the latter is measured in atomic units, say ($e^2/m_e c^3$), then the constant of proportionality is of order unity. Following Dirac, other fundamental 'constants' were speculated to vary with time: for example, Teller [2] proposed $\alpha = e^2/hc \sim (\log t)^{-1}$ for the fine-structure constant whereas Gamov [3] discussed the option $\alpha \sim t$. Dyson [4] has twice reviewed the experimental evidence for the time variation of the fundamental constants. Whereas a changing G is possible within the experimental uncertainties, α seems to have been constant throughout the history of the universe.

In recent discussions of the anthropic principle (for reviews see, e.g., Carr and Rees [5] and Breuer [6]) the possibility of changing fundamental constants—changing in time and/or in different parts of the universe and/or in different universes of Wheeler's [7] infinite ensemble of universes—has again been raised, the opinion being expressed that only those universes where the fundamental constants are 'right', namely have precisely the values of our universe now, are 'cognisable'. In this connection Ellis and Kreuzer [8] have pointed out that changing α would affect in particular the chemistry of medium and heavy elements as their structure and bonding properties

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are sometimes altered quantitatively by relativistic corrections even at the present value of α . We list a few striking examples [9]: (i) the chemical difference between fifth- and sixth-row elements, for example the monovalency of Tl; (ii) the contraction of bond lengths in the series BH, AlH, GaH, InH, TlH by as much as 7%, as in the CuH to AuH series; (iii) the gold 'anomaly', i.e., the shift between s and d levels with resulting larger ionisation potential and electron affinity; (iv) peculiarities in the bonding properties for Pb and Hg caused by strong p-wave admixtures, etc. It goes without saying that such relativistic effects would be quantitatively and even qualitatively different if α were varying. With a smaller α these effects would be absent; a larger α would not only enhance them but generate more of the same in medium-weight atoms. The implications as to toxicity for living organisms are obvious.

To go beyond such qualitative discussions we decided to study relativistic corrections in a medium-weight atom as a function of α . We chose Fe in the light of its important role in biological molecules. We recall that Fe occurs, for example, in haemoglobin in the ionised forms Fe^{2+} and Fe^{3+} . The question could then be asked: how different must α be in order to change the electronic level structure and the valence directions of these two species? For both Fe^{2+} and Fe^{3+} ions we have performed relativistic Hartree-Fock (SCF Dirac-Fock) calculations using Desclaux's program [9] to determine the large and small components of the radial part of their wavefunctions. Since the angular parts of the valence spinors $3D^*$ and $3D$ are fixed, only the radial wavefunctions are α dependent [3]. In the case of Fe^{2+} the calculations have been performed for the ground state in addition to the $(3D^*)^4 3D^1 4S^1$ and $(3D^*)^3 3D^1 4S^1 4P^*$ excited configurations, respectively, which play an important role in the formation of directed valences of an Fe^{2+} ion in haemoglobin. (Here the capital letters P, D with an asterisk always have the lower j value and those without an asterisk the higher j value, that is $3D^* = 3d_{3/2}$, $3D = 3d_{5/2}$ and $4P^* = 4p_{1/2}$, respectively.) In the course of these computations we have chosen $\alpha = 0.2\alpha_0$, $0.5\alpha_0$, α_0 , $2\alpha_0$ and $5\alpha_0$, where α_0 is the present value of the fine-structure constant. Significant changes result only at the largest value of α chosen, as we will see below. By implication one expects much larger changes for fifth- and sixth-row elements as the strength of the relativistic corrections is related to the parameter αZ . However, one must keep in mind that for a point-charge nucleus there are no bound states with $j = \frac{1}{2}$ for $\alpha Z > 1$ and that the 1s binding energy increases rapidly as αZ approaches one from below. Thus for $\alpha = 5\alpha_0$ one cannot obtain SCF solutions for Ni, Cu and heavier elements without taking the finite nuclear size into account [10, 11]. Moreover, for $\alpha Z \sim 1.24$ the 1s binding energy exceeds $2mc^2$ so that the 1s state becomes embedded in the lower positron continuum rendering the neutral charge vacuum unstable. Whereas this happens for α_0 at $Z \sim 170$, i.e., well above the heaviest naturally occurring isotopes, for $\alpha = 5\alpha_0$ it would limit the heaviest elements to the range $Z = 30-40$. Thus heavier elements could only have been produced during the cosmological evolution at times when α was not much larger than its present value α_0 . The calculations on Fe will allow us to make this statement somewhat more quantitative.

2. Results and their discussion

In table 1 we present the one-electron energies (in atomic units) for the ground state and for the two excited configurations of Fe^{2+} mentioned above. As we can see, in the range $\alpha = 0.2\alpha_0-2\alpha_0$ all the levels hardly change in the ground state. Only at

Table 1. Orbital energies of Fe²⁺ (in -au).

α/α_0	0.2	0.5	1	2	5	
Level						
1S	262.166	262.670	264.503	272.36	388.38	
2S	32.642	32.748	33.134	34.808	62.284	
3S	4.851	4.868	4.931	5.205	9.758	
2P*	28.153	28.237	28.543	29.865	50.148	(3D*) ⁴ (3D) ²
2P	28.086	28.074	28.030	27.834	24.779	configuration
3P*	3.540	3.553	3.597	3.789	6.838	(ground state)
3P	3.371	3.371	3.369	3.362	3.137	
3D*	1.289	1.288	1.283	1.265	1.125	
3D	1.264	1.262	1.252	1.213	1.021	
1S		262.962	264.789	272.628		
2S		33.076	33.456	35.106		
3S		5.151	5.211	5.471		
2P*		28.570	28.870	30.166		
2P		28.388	28.338	28.120		(3D*) ⁴ 3D ¹ 4S ¹
3P*		3.847	3.888	4.067		configuration
3P		3.613	3.608	3.584		
3D*		1.566	1.558	1.521		
3D		1.532	1.518	1.461		
4S		0.935	0.941	0.969		
1S		263.347	266.562	272.992	388.511	
2S		33.502	34.172	35.514	62.553	
3S		5.503	5.607	5.816	10.079	
4S		1.063	1.075	1.098	1.673	
2P*		28.984	29.510	30.563	50.396	
2P		28.814	28.718	28.527	25.072	(3D*) ³ 3D ¹ 4S ¹ 4P ^{*1}
3P*		4.144	4.215	4.358	7.125	configuration
3P		3.962	3.947	3.918	3.363	
4P*		0.800	0.806	0.819	1.090	
3D*		1.911	1.891	1.850	1.375	
3D		1.884	1.854	1.795	1.246	

Table 2. The large component of the radial wavefunctions of Fe²⁺ in its ground state ((Ar)(3P*)²(3D*)⁴(3D)²) as a function of α/α_0 .

α/α_0	r (au)	0.1	0.5	1.0	1.35	1.5	2.0	2.46	3.0
3D state	0.2	0.6955 [†]	8.4705	8.6723	6.7791	6.0164	3.6899	2.3326	1.2852
	0.5	0.6943	8.4580	8.6706	6.7842	6.0232	6.6991	3.3410	1.2916
	1	0.6900	8.4128	8.6643	6.8023	6.0475	2.7321	2.3714	1.3145
	2	0.6715	8.2261	8.6351	6.8738	6.1448	3.8671	2.4967	1.4100
	5	0.4908	6.6283	8.2942	7.3252	6.8000	4.8422	3.4330	2.1552
3P* state	0.2	-5.2559	8.7810	9.5885	5.7701	4.5199	1.6798	0.6772	0.2151
	0.5	-5.2760	8.8218	9.5741	5.7488	4.4997	1.6680	0.6711	0.2128
	1	-5.3482	8.9684	9.5212	5.6719	4.4269	1.6257	0.6496	0.2045
	2	-5.6355	9.5665	9.2836	5.3491	4.1253	1.4564	0.5654	0.1730
	5	-5.9566	13.697	5.5556	2.1637	1.4482	0.3274	0.0970	0.0253

[†] Each value in the table is multiplied by 10 (that is, the large radial component of the 3D function at $\alpha/\alpha_0 = 0.2$ and $r = 0.1$ au has the value 0.06955).

Table 3. The large component of the radial wavefunctions of Fe^{2+} in its $3D^*3D^14S^4P^*$ excited configuration as a function of α/α_0 .

α/α_0	r (au)	0.1	0.5	1.0	1.35	1.5	2.0	2.46	3.0	4.0	5.0	6.0	7.0
3D* state	0.5	0.7823†	9.3648	8.8863	6.3345	5.3766	2.7399	1.4619	0.6556	0.1322			
	1	0.7890	9.3349	8.8823	6.3517	5.3992	2.7681	1.4853	0.6705	0.1369			
	2	0.8024	9.2750	8.8743	6.3862	5.4443	2.8245	1.5321	0.7011	0.1464			
	5	0.7744	8.1228	8.8253	6.9508	6.1916	3.7986	2.3779	1.2861	0.3579			
	0.5	0.7790	9.3475	8.8946	6.3513	5.3926	2.7433	1.4552	0.6439	0.1236			
3D state	1	0.7717	9.2775	8.8998	6.3945	5.4434	2.7963	1.4961	0.6689	0.1310			
	2	0.7571	9.1375	8.9102	6.4810	5.5449	2.9023	1.5778	0.7190	0.1457			
	5	0.5496	7.3444	8.7291	7.2795	6.5818	4.2231	2.7300	1.5321	0.4574			
	0.5	0.8106	-3.0711	0.2851	4.4328	5.6235	7.4823	6.9748	5.3699	2.4508	1.0684	0.3453	0.1173
	1	0.8877	-3.1503	0.4556	4.6033	5.7704	7.5171	6.9371	5.2922	2.3825	1.0285	0.3289	
4S state	2	1.0419	-3.3087	0.7965	4.9422	6.0643	7.5866	6.8618	5.1368	2.2459	0.9487	0.2960	0.0977
	5	2.8269	-3.5173	6.7594	8.8504	8.7554	6.5546	4.3404	2.3597	0.6067	0.1704	0.0033	0.0074
	0.5	1.5862	-2.6943	-0.4181	2.9001	4.0124	6.4621	6.8375	6.0715	3.5820	1.9225	0.7938	0.3337
	1	1.6180	-2.7467	0.2807	3.0378	4.1410	6.5257	6.8453	6.0325	3.5222	1.8770	0.7692	
	2	1.6817	-2.8514	-0.0058	3.3133	4.3983	6.6528	6.8588	5.9546	3.4026	1.7861	0.7199	0.2967
5	1.7728	-3.1214	4.2616	7.0930	7.5718	7.3102	5.9286	4.0867	1.6269	0.6538	0.1953	0.0626	

† Each value in the table is multiplied by 10.

$\alpha = 5\alpha_0$ can we detect larger changes in the level positions as compared with the case $\alpha = \alpha_0$. One finds a similar situation in the two excited configurations also: the one-electron energy is very similar for all levels in going from $\alpha = 0.5\alpha_0$ to $\alpha = 2\alpha_0$, and again one finds larger changes only at the large value $\alpha = 5\alpha_0$ for the second calculated excited configuration. Since the dependence of the level positions on the value of α is very similar in the case of the Fe^{3+} ion, we do not present detailed results on these levels here.

In table 2 we show the large component of the radial wavefunctions of Fe^{2+} for the 3D and 3P* states in the ground-state electronic configuration ($\dots(3D^*)^4(3D)^2$) of this ion. We can see that the value of the wavefunction in both cases remains practically unchanged in the whole range of r investigated when we go from $\alpha = 0.1\alpha_0$ to $\alpha = 2\alpha_0$. Again we discover a more considerable change only at large values of α ($\alpha = 5\alpha_0$) and at larger distances from the nucleus ($r \geq 2$ au). We do not show the values belonging to the 3P and 3D* states in this table because according to our detailed results the change in these states as a function of α/α_0 is even smaller than in the 3D and 3P* states. We also do not give here the corresponding results for the small radial component of the states discussed, because their numerical values are generally a factor between 10^3 and 10^2 smaller than those of the corresponding large component and therefore their change with α is completely negligible.

In table 3 we give the large components of the radial wavefunctions for Fe^{2+} in its $(3D^*)^3 3D^* 4S^1 4P^* 1$ excited configuration for all the four one-electron states involved as a function of α/α_0 and r . As we see from this table, the change in the values of these wavefunctions is again small between the values of $\alpha/\alpha_0 = 0.5$ and 2.0, respectively. The comparatively largest changes at the 4S and 4P* radial functions are found in the region $0.5 \text{ au} \leq r \leq 2.0 \text{ au}$. In accordance with the results obtained for the ground state, one again finds significantly large changes in the function only for the large value $\alpha = 5\alpha_0$. One should mention that the small components again have values two or three orders of magnitudes smaller. Therefore in this case also we do not show detailed results for them.

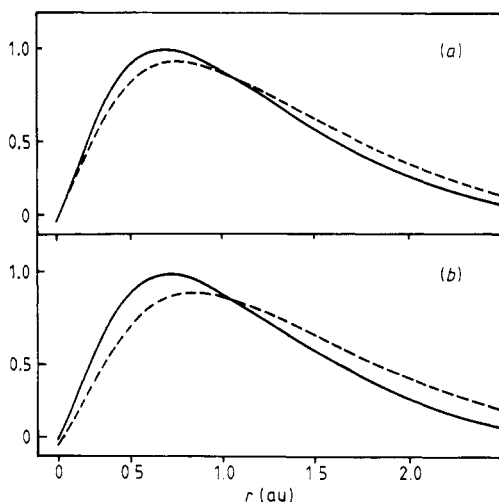


Figure 1. (a) The large radial component of the 3D* wavefunction of Fe^{3+} as a function of r (in au): full curve, $\alpha/\alpha_0 = 1$; broken curve, $\alpha/\alpha_0 = 5$. (b) As (a), but for the 3D state of Fe^{3+} .

Turning to the Fe^{3+} ion, we can see in figure 1 the curves for the large components of the 3D and 3P* wavefunctions in the $(3D^*)^4 3D^1$ ground states at different values of α/α_0 and r . In figure 2 we represent the corresponding curves for the 3D and 3P* states in the $(3D^*)^4 (3D)^2$ ground states for Fe^{2+} . A comparison of the two sets of curves indicates that they are identical to a very good approximation. This means that in the case of the Fe^{3+} ion also a change in the value of the fine-structure constant does not change the electronic structure of Fe^{3+} nor the directionality of its valences.

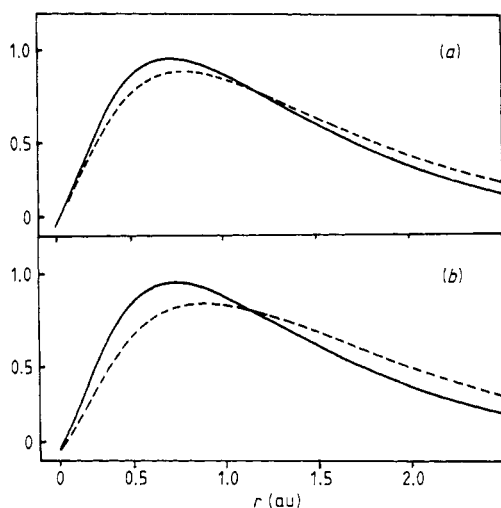


Figure 2. As figure 1, but for the large radial components of the 3D* (a) and 3D (b) wavefunctions of Fe^{2+} .

3. Conclusions

According to Teller's hypothesis [2], the fine-structure constant has changed only at the per cent level between the time life first appeared on Earth and the present. Gamov [3], on the other hand, postulated that in this time span α had increased by about 25%. None of these changes affect the chemistry of iron but, as indicated in the introduction, a great deal of care must be exercised with the heavier elements. We note that for Fe and for $\alpha = 5\alpha_0$ the key parameter αZ , which is a measure of the relativistic corrections, is about 0.9. Thus one expects drastic changes in the chemistry of, for example, Cd for $\alpha \sim 2.5\alpha_0$ and for Pb already at $\alpha \sim 1.5\alpha_0$. Although, according to Dyson [4], there is no evidence that α was different in the past, our findings confirm the suspicion that in discussions of other worlds [5-7] and of physics and biology in an open universe [12] some attention should also be paid to chemistry.

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