Model Calculations on the Influence of Quantum Electrodynamical Effects on the Chemistry of Superheavy Elements. The Chemistry of Element E184

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Using a phenomenological model, the influence of quantum electrodynamical effects on the prediction of the chemical behavior of superheavy elements within a relativistic Dirac–Slater calculation was investigated. This influence will be small and nondetectable for elements up to $Z = 114$. For elements near $Z = 164$ some changes in the ground state configurations occur but the chemical behavior will not change. Using this heuristic model, it is also possible to calculate elements beyond $Z = 175$. As an example we have chosen element E184 and are now able to make more valid speculations about the chemical behavior of the element than Penneman and co-workers could.

I. INTRODUCTION

The development of self-consistent Dirac–Slater[1,2] and Dirac–Fock[3] computer programs in the last years and their application to superheavy elements have lead to quite a detailed prediction[4–6] of the chemistry of the yet unknown superheavy elements up to element E172. The difference in total energy between different electron configurations in the atoms and ions, the systematics of the energy eigenvalues and the radial distribution of the outer electrons have been the basis for these predictions. This can be done because these programs reproduce the most stable electron configurations as well as ionization potentials and radii for the heavy known elements quite well.

The Dirac–Fock calculations by Mann[7] have already shown that the two improvements in comparison to Dirac–Slater calculations, namely, the exact treatment of the exchange term and the contribution from the magnetic interaction and retardation terms (sometimes together they are called the Breit interaction) between the electrons lead only to small changes in the energy eigenvalues and ionization potentials. This is true even for the elements around E164. The filling of the shells and the chemical interpretation remains unchanged when these improvements are included. This result is not too astonishing because both corrections are only relatively small and depend on the interaction of the electrons with themselves only.

Besides these contributions from an advanced treatment of the electron–electron interaction, one expects corrections coming from the interaction of the electrons with the vacuum (vacuum polarization) and the zero-point electromagnetic field (vacuum fluctuation). Both effects depend strongly on the nuclear charge and their usual description is given in an expansion in $Z\alpha$ (where $\alpha = 1/137$).

We would like to discuss here the influence of these quantum electrodynamical effects on the chemistry of the superheavy elements near the two expected[8] islands of quasistability, namely, near $Z = 114$ and $Z = 164$.

II. DESCRIPTION OF VACUUM FLUCTUATION AND VACUUM POLARIZATION

It is not clear whether the Dirac equation, which up to now is the best known relativistic single particle equation, describes the inner electrons in heavy atoms correctly. Besides this principal uncertainty, the effects of vacuum polarization and vacuum fluctuation are expected to have a strong influence on the energy eigenvalues of the inner electrons and hence indirectly on the valence electrons, which might in turn cause a change in the expected chemical behavior.

The effect of vacuum polarization in heavy muonic atoms is well established up to the second order in the usual expansion parameter[9,10] $Z\alpha$, whereas for such atoms, the effect of fluctuation is very small. The opposite is true for electronic atoms. In the Lamb shift of hydrogen, for example, the effect of fluctuation leads to a contribution of more than 1000 MHz, whereas the effect of vacuum polarization contributes only by -27 MHz. Very recently, Desiderio and Johnson[11] calculated the vacuum fluctuation contribution for elements around mercury according to a method developed by Brown et al.[12] Their result for the 1s level of Hg for the vacuum fluctuation is about 15 Ry whereas vacuum polarization is of the order of -3 Ry. The 15 Ry result was also obtained very recently by Erickson[13] based on an extension of the method used for calculation of the Lamb shift for small atomic numbers. This has to be compared with about -6140 Ry from the electrostatic contribution, 23 Ry from the magnetic interaction, -1.5 Ry from the retardation, and about -0.1 from the correlation, as obtained by Mann and Johnson.[14] They reproduced the experimental ionization energy of the innermost electron of various heavy atoms with an accuracy of about 5 eV. This result shows that the quantum electrodynamical contributions in these elements are relatively small and that the Dirac equation and the usual linear description of the electromagnetic field are fully valid in this region.[15]

If we go to the superheavy elements, the inner

TABLE I. The somewhat overestimated corrections of vacuum fluctuation and the correction for vacuum polarization of the order $Z\alpha$ for the 1s and 2s levels for the elements E110, E112, and E114 in rydberg.

Element	Level	δr (fm)	Fluctuation (Ry)	Polarization (Ry)
110	1s	8.9	+87	−19.4
	2s		+18	−3.6
112	1s	8.8	+101	−22.3
	2s		+21	−4.3
114	1s	8.7	+115	−25.3
	2s		+24.7	−5.1

electrons will be bound so strongly that near element E175, the energy eigenvalues according to the solution of the Dirac equation (even after taking into account the effect of the extended nucleus)[6] will be smaller than $-2mc^2$. Other calculations[16] which do not take into account the effect of the electron cloud indicate that the critical atomic number is about 165. This means that the electrons are energetically degenerate with electrons in the lower continuum. This behavior is physically not currently understood. One possible explanation is that the energy eigenvalues might approach the lower continuum only asymptotically.[17] Starting from the Bethe–Salpeter equation, Reinhardt et al.[18] have given a mathematical description of the atomic electrons together with the vacuum. However, real calculations have not yet been made. These authors also show that the whole difference between the Bethe–Salpeter and the usual Dirac–Fock description is mainly given by expressions which for low Z, degenerate to the usual expressions of vacuum polarization and fluctuation.

We have recently proposed a very simple phenomenological description of the effect of vacuum fluctuation[19] which is easy to handle and leads to the right order of magnitude for this contribution for the low lying ns levels of the atoms. The main idea is that the electrons do not feel the usual potential at a point r but feel rather an effective potential which can be constructed by averaging the usual potential within a volume at point r with radius δr. Here δr is the so called "Zwitterbewegungsamplitude" which comes from the interaction of the electrons with the zero point electromagnetic field as described by Bjorken and Drell.[20] This model describes a partial leveling off of the single particle energies of the strongest bound electrons due to a drastic change of the potential in the vicinity of the nucleus.

We are able to assess how large its influence would be on the chemistry of heavy and superheavy elements by introducing this reduced potential into a self-consistent Dirac–Slater program.[1] We assume in this

heuristic study that this effective potential near the nucleus might be an adequate description of the expected effect of vacuum fluctuation. For the calculations of the elements below E120 we also have added to the potential which arises from the extended nucleus, the exact expression for the vacuum polarization potential, of the order $Z\alpha$. This is given for the extended nuclear charge distribution in Ref. 9 and remains the leading term, even for these high Z elements. Because the vacuum polarization correction is given only up to now in an expansion in $Z\alpha$, respectively α, we have not included this effect in the calculations for elements beyond. This can be justified because even for element E120 the vacuum polarization contribution will be only of the order of about 30% of the vacuum fluctuation contribution. Secondly, it is expected that the next higher order term, which depends on $(Z\alpha)^3$ and which has the opposite sign, will reduce the total effect of vacuum polarization considerably. Thus we use this phenomenological description for very high Z as the description for all the quantum electrodynamical effects.

III. RESULTS

The present calculations show only very small changes in the differences between the total energies of the lowest lying electron configurations obtained with and without this treatment of the quantum electrodynamical effects. This finding applies for the elements on the first island of the expected stability near E114. This inclusion reduces the differences between the total energies of different electron configurations of an element between 1% and 20% depending on the valence electron configurations. These small changes show that the expected chemical behavior will not change in any of these elements. The influence on the energy eigenvalues and principal maxima of the outer electrons is also very small even if these electrons have a nonnegligible density near the nucleus, which, for example, is true for the 8s electrons in the elements E119 and E120. The energy eigenvalue of these electrons increases by only 1% and the radius of their principal maxima by 3%.

Although the chemical behavior of the elements near E114 is not expected to change compared with the predictions given in Refs. 4 and 6, the influence of the quantum electrodynamical effects will be detectable in many other physical quantities such as the ionization energies or the x-ray spectra of the inner electrons. Table I shows the contribution of these effects to the binding energies for 1s and 2s electrons of the elements E110, E112, and E114 as well as the values of δr which were used. We estimate that the present contribution due to fluctuation is too large by nearly a factor of 2 compared with the extrapolation made from the more exact calculations of Johnson et al.[11] By using this probable overestimation we are

TABLE II. The differences in the total energies for the lowest lying electron configurations of the elements E159, E160, and E165–E170 with and without the quantum electrodynamical corrections in rydberg.

Element	Configuration[a]				Differences without the corrections[b]	Differences with the corrections
	$7d_{5/2}$	$9s_{1/2}$	$8p_{3/2}$	$9p_{1/2}$		
E159	...	1	...	...	0.0	0.0
	1	...	...	...	0.063	0.015
E160	1	1	...	...	0.0	0.033
	2	...	...	...	0.019	0.0
	...	2	...	...	0.074	0.207
E165	6	1	...	...	0.0	0.0
	6	...	1	...	0.083	0.041
	6	...	...	1	0.102	0.085
E166	6	2	...	...	0.0	0.0
	6	1	...	1	0.098	0.059
	6	1	1	...	0.114	0.024
	6	...	2	...	0.188	0.071
E167	6	2	...	1	0.0	0.079
	6	2	1	...	0.002	0.0
E168	6	2	...	2	0.0	0.145
	6	2	1	1	0.008	0.090
	6	2	2	...	0.015	0.0
	6	1	3	...	0.179	0.020
E169	6	2	1	2	0.0	0.142
	6	2	2	1	0.040	0.086
	6	2	3	...	0.070	0.0
E170	6	2	2	2	0.0	0.122
	6	2	3	1	0.071	0.066
	6	2	4	...	0.141	0.0

[a] Plus E118 core$+8s^2 8p_{1/2}^2 5g^{18} 6f^{14} 7d_{3/2}^4$.

[b] Reference 6 for E165 to E170 and Ref. 21 for E159 and E160.

sure to be on the safe side when estimating the change in chemical behavior due to the quantum electro-dynamical effects.

For higher elements, Erickson[13] has calculated values for the 1s electronic vacuum fluctuation for the elements E137 and E1000. His values agree with our values within the very large error bars given by him. Therefore we assume as a first approximation that our simple description will give the right order of magnitude for the influence of this effect on the outer electron shells. By changing the value of δr we are also able to vary the strength of the effect and to obtain an idea about the influence on the outer electron shells as function of δr. In Table II we summarize the differences in the total energies between the lowest lying electron configurations for some elements in the region of the second quasistable island near E164 (using δr values from 6.7 fm for E160 to 6.4 fm for E170). The first difference[21] in orbital occupation occurs at element E160 where the 9s electron disappears from the ground state and instead a second $7d_{5/2}$ electron occurs. This change will also be true in the case of much smaller quantum electrodynamical effects (i.e., smaller δr) because the difference in the total energies between the configurations $7d^5\,9s$ and

$7d^6$ was already very small. The inclusion of quantum electrodynamical effects is unimportant in the case of E159 where the $7d^4\,9s$ electronic configuration remains the most stable one.

The second change in the order of the filling occurs between the elements E167 and E172. Contrary to Refs. 6 and 7, where the $9p_{1/2}$ electrons were predicted to occur in the ground state before the $8p_{3/2}$ orbitals were occupied, the filling of these both shells is now interchanged. This can be understood also in terms of a reduced direct relativistic effect on the $9p_{1/2}$ electrons. Nevertheless the energy eigenvalues and outer radial distribution of the wavefunctions of both shells remain very near to each other and both would be easily available for chemical bonding. Hence the chemical behavior and the main oxidation states will be the same as in Ref. 6. These elements E167 to E172 were predicted to be the p elements of the ninth period. Also for E159 and E160, no change in the chemical behavior is expected. Both the $7d_{5/2}$ and 9s electrons, which compete with each other, have very small ionization energies and are radially extended quite far. Hence their main oxidation states will remain 1 and 2, respectively.

This negative result in the investigation of the

TABLE III. The total energies (in rydberg) for the lowest lying electron configurations of element E184 in its ground state and the lowest lying configurations and their ionization energies for some ions.

	Orbital occupation number[a]								$-E$(Total) (Ry)	$\Sigma\Delta E$(Ionization) (Ry)
	$9s$	$9p_{1/2}$	$8p_{3/2}$	$6g$	$7f$	$8d$	$10p$	$10s$		
E 184	2	2	4	5	4	3	...	...	463 204.551	0
	2	2	4	5	5	2	...	...	4.539	
	2	2	4	5	3	4	...	...	4.502	
	2	2	4	5	6	1	...	...	4.481	
	2	2	4	5	4	2	...	1	4.457	
	2	2	4	5	5	1	1	...	4.443	
	2	2	4	5	6	...	1	...	4.404	
E 184^{+1}	2	2	4	6	3	2	...	...	463 204.333	0.218
E 184^{+2}	2	2	4	6	4	...	...	...	463 203.526	1.025
E 184^{+3}	2	2	4	6	3	...	...	...	463 202.068	2.483
E 184^{+4}	2	2	4	7	1	...	...	...	463 199.786	4.765
E 184^{+5}	2	2	4	7	...	...	...	...	463 196.668	7.883
E 184^{+6}	2	2	4	6	...	...	...	...	463 192.358	12.193
E 184^{+8}	1	2	4	5	...	...	...	...	463 179.651	24.900
E 184^{+10}	...	1	4	5	...	...	...	...	463 162.701	41.850

[a] Plus E164 core.

possible changes in the chemical behavior caused by introducing quantum electrodynamical effects indicates that the inner electrons are (strongly) decoupled from the outer electrons and that a change in the potential of 50% or more, in the vicinity of the nucleus, has virtually no influence on the expected chemical behavior of the elements as far as we are able to predict the chemistry of these elements up to now.

IV. THE CHEMISTRY OF ELEMENT E184

With the present description of the atom where the binding energy of the 1s electrons is sharply decreased, it is possible to calculate elements beyond E175. Penneman et al.[5] speculated about the chemistry of element E184 although calculations of neither the nuclear stability nor the atomic structure were available to them. Therefore we have chosen this element E184 as an example for calculation. Although we had to use a δr value of 15 fm, which is nearly a factor 3 larger than the value extrapolated in Ref. 18, we think that we still obtain a valuable answer as long as we are concerned with the chemical behavior of this element. Somewhere beyond the noble element E172, another very long transition series is expected to occur. The electrons of the $10s$, $10p_{1/2}$, $9p_{3/2}$, $8d_{3/2}$, $7f_{5/2}$, $7f_{7/2}$, $6g_{7/2}$, and $6g_{9/2}$ shells could be the next series of electrons available for bonding. The results of the calculations for the ground state and different ionization states of E184 are given in Table III. In the ground state configuration of E184, namely, E172 core + $6g^5$ + $7f^4$ + $8d^3$, no new s or p electrons occur, which indicates that the filling in this region will be simpler than at the beginning of the superactinides which start near E121 where there are often four incomplete

subshells. This is of course mainly a result of the effective potential near the nucleus which hinders the binding of the ns and $np_{1/2}$ electrons.

Figure 1(a) shows the radial dependence of the outer electron wavefunctions of the neutral E184 atom. The $8d$ electrons will be easily oxidized because of their small ionization energies and their radial extension. But Table III indicates that on the way to higher oxidation states the occupation of the $6g$ and $7f$ shells changes. The main trend is clearly an increase in the number of electrons in the $6g$ shell; the latter is radially so far inside the atom that these electrons will not be directly available for chemical bonding. It is observed that the $7f$ electron wavefunction has a very long tail for large r, so instead these electrons will become involved in chemical bonding. This prediction can be made because the radial and energetical configuration of the outer electrons is very analogous to the elements of the early actinide series. As an example, we give in Fig. 1(b) the outer wavefunctions of uranium for comparison. In uranium we have three outer electrons in open shells ($7s^26d^1$) which will be removed easily. But also the $5f$ electrons are available for bonding because of their long tail at large r which leads to a maximum 7+ oxidation state for uranium. When the tail of the $5f$ wavefunction becomes smaller for larger Z, then the maximum oxidation state will be also reduced; this occurs in the heavier actinides. For element E184, this comparison means that the oxidation states 5+ (or 6+) when all available $8d$ or $7f$ electrons are ionized may be reached easily. Using two formulas given by Jørgensen[22,5] which connect the ionization energies and the most stable ion in aqueous solution, one can expect to find mainly the

4+ ion in aqueous solution. This result is obtained using a value for the so called "hydration difference" parameter between 25 and 30 kK. To reach higher oxidation states than 5+ or 6+ there are two possibilities. Either some $6g$ electrons have to be removed which is not very likely (a) because we know from the inactive behavior of the deeply buried analogous $4f$ electrons in the lanthanides that they are (nearly) not oxidized and (b) because the binding energy of the $6g$ electrons increases rapidly in the higher oxidation states. The alternative possibility is to involve some of the outer $9s$, $9p_{1/2}$, or $8p_{3/2}$ electrons in the chemical bonding. This is also very unlikely because these are closed shells and their ionization energy is relatively large. It is the same order of magnitude as, for example, that of the outer $6s$ or $6p$ electrons in uranium ions which we know are never involved in chemical bonding. In the higher ionization states the calculations lead also to another interesting result. (See Table III.) The binding energy in the open $6g$ shell becomes so large, beginning with the 8+ state, that it is energetically better for some of the outer electrons in the outer closed $9s$, $9p_{1/2}$, and $8p_{3/2}$ shells instead to occupy the open $6g$ shell. This is the first time that such an unusual behavior of the occupation of an open shell leads to the deoccupation of closed shells. From the ionization potentials in Table III we also see that the oxidation state 10+ with a total ionization energy of 41.8 Ry is energetically already outside the range of present chemical experience. This clearly indicates that also here in a region of a very long transition series where many outer electron shells are filled simultaneously in the neutral atom, the increase in ionization energy is almost similar to what is observed in all other elements, which means that we do not expect extremely high or unusual oxidation states.

V. CONCLUSION

In conclusion one may say that although we have introduced only a very rough description which simulates the effects coming from quantum electrodynamics, the results are expected to be in the right direction and of the right order of magnitude; in most cases, they may be even too large. We found that neither the direct effect of a drastic change of the potential near the nucleus nor the indirect influence through the change of the inner electrons influences the outer electrons sufficiently to produce a significant change in the filling of the outer valence electrons. The only difference in the filling of the shells will be the interchanged order of filling of the $9p_{1/2}$ and $8p_{3/2}$ electrons and the removal of the $9s$ electron in E160; but this will not change the chemistry of these elements. This negative result of the calculations gives us also more confidence in the predictions of the chemical behavior of the superheavy elements and it clearly
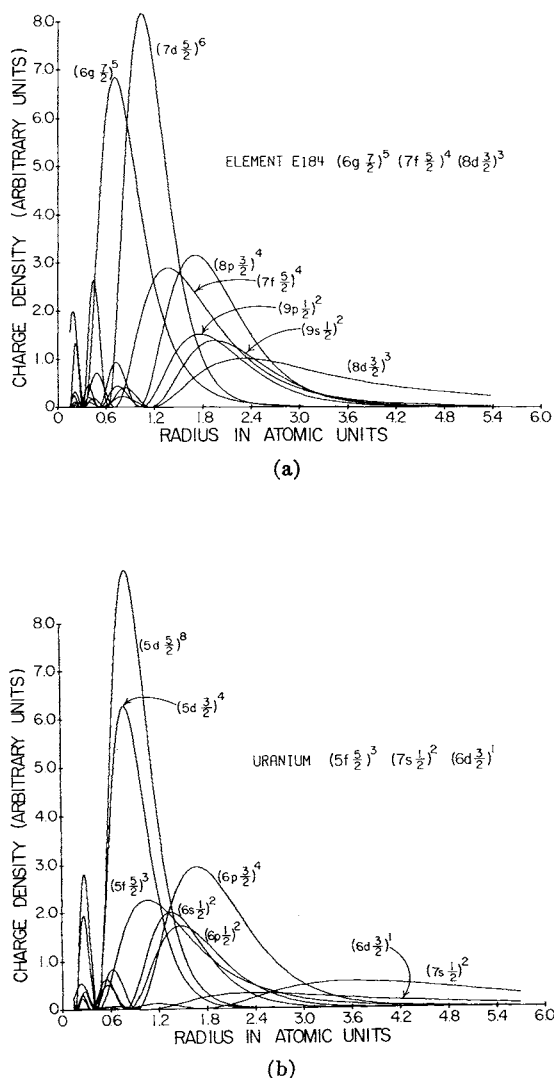

Fig. 1. Calculated radial charge densities of the outer electron shells of (a) element E184 and (b) of uranium for comparison.

shows that they can be trusted at least for the elements in the first island of stability near E114.

The calculations also show that some early speculations, namely, that different nuclei of different isotopes but the same element could produce different chemical behavior in the region of superheavy elements, will not be true. Besides the fact that these nuclei are expected to be spherically symmetric, a large nuclear quadrupole moment might influence only the inner electrons; but an effect on the chemical behavior of these elements now seems very unlikely.

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