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Ground State Electron Configuration of Rutherfordium: Role of Dynamic Correlation

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The low-lying electronic states of Rf^+ and Rf are investigated by the relativistic coupled cluster method based on the Dirac-Coulomb-Breit Hamiltonian. A large basis set $(34s24p19d13f8g5h4i)$ of Gaussian-type orbitals is used. The external 36 electrons are correlated. In contrast with recent multiconfiguration Dirac-Fock (MCDF) results, the $7s^26d^2\,{}^3F_2$ state is found to be the ground state of the atom, lying about 0.30 eV below the $7s^27p6d\,{}^3D_2$ state (the MCDF ground state). The dynamic correlation of the system, requiring virtual orbitals with l up to 6, is responsible for the reversal. The first ionization potential of the atom is predicted at 6.01 eV.

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The chemistry of the heaviest known elements ($Z > 100$) is a subject of considerable recent interest [1]. Experiments on these systems are difficult, since only a few atoms are available to the researcher, and even such fundamental questions as the ground state configuration remain unsolved in many cases. A particularly interesting case is that of Rf, element 104, which is the first atom after the actinide series. In analogy with the lighter group 4 elements, Rf should have the ground state configuration $[\mathrm{Rn}]5f^{14}6d^27s^2$. Keller [2] suggested that the relativistic stabilization of the $7p_{1/2}$ orbital would yield a $7s^27p_{1/2}^2$ ground state. Recent multiconfiguration Dirac-Fock (MCDF) calculations [3,4] found that the $2p^2$ state was rather high; they indicate a $6d7s^27p$ ground state, with the lowest state of the $6d^27s^2$ configuration higher by 0.5 [3] or 0.24 eV [4]. The two calculations are similar, using numerical MCDF [5] in a space including all possible distributions of the four external electrons in the $6d$, $7s$, and $7p$ orbitals, and the difference may be due to the different programs used or to minor computational details. These MCDF calculations take into account nondynamic correlation only, which is due to near-degeneracy effects and can be included by using a small number of configurations. A similar approach by Desclaux and Fricke [6] gave errors of 0.4–0.5 eV for the energy differences between $(n-1)d$ and np configurations of Y, La, and Lu, with the calculated np energy being too low. Desclaux and Fricke corrected the corresponding energy difference in Lr by a similar amount [6]. If a shift of similar magnitude is applied to the MCDF results for Rf, the order of the two lowest states may be reversed. It should also be noted that dynamic correlation, largely omitted from MCDF, has recently been shown to play a significant role in determining atomic excitation energies [7], reducing the average error in calculating Pr^{+3} excitation energies by a factor of 4 relative to MCDF results. This was achieved using the relativistic coupled cluster (RCC) method. Other recent applications of the method gave accurate transition energies for U^{+4} [7], Au [8], 2–5 electron ions [9], and the alkali atoms Li–Fr [10]. The method is applied here to the interesting problem of the Rf ground state.

The RCC method with single and double excitations includes relativistic and correlation effects simultaneously to high order. A detailed description of the method may be found in earlier papers [7–10], and only a brief account is given here. We start from the projected Dirac-Coulomb (DC) or Dirac-Coulomb-Breit (DCB) Hamiltonian [11,12]

$$H_+ = \Lambda^+\left[\sum_i [c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_{\mathrm{nuc}}(i)] + \sum_{i<j}(V_{\mathrm{eff}})_{ij}\right]\Lambda^+. \tag{1}$$

The nuclear potential V_{nuc} includes the effect of finite nuclear size. Λ^+ is a product of projection operators onto the positive energy states of the Dirac Hamiltonian. The Hamiltonian H_+ has normalizable, bound state solutions. Equation (1) is the no-virtual-pair approximation, with virtual electron-positron pairs not allowed in intermediate states. The effective potential in the Coulomb gauge, correct to second order in the fine-structure constant α, is the Coulomb-Breit potential [13]

$$V_{\mathrm{eff}} = \frac{1}{r_{12}} - \frac{1}{2r_{12}}\left[\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})/r_{12}^2\right], \tag{2}$$

where the second term is the frequency-independent Breit interaction.

In q-number theory the DCB Hamiltonian H_+ is rewritten in terms of normal-ordered products of the spinor operators $\{r^+s\}$ and $\{r^+s^+ut\}$ [11,14]

$$\begin{aligned} H &= H_+ - \langle 0|H_+|0\rangle \\ &= \sum_{rs} f_{rs}\{r^\dagger s\} + \frac{1}{4}\sum_{rstu}\langle rs||tu\rangle\{r^\dagger s^\dagger ut\}, \end{aligned} \tag{3}$$

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where f_{rs} and $\langle rs||tu\rangle$ are, respectively, elements of one-electron Dirac-Fock and antisymmetrized two-electron Coulomb-Breit interaction matrices over Dirac four-component spinors. The effect of the projection operator Λ^+ is now taken over by normal ordering, denoted by the curly braces in the equation above, which requires annihilation operators to be moved to the right of creation operators as if all anticommutation relations vanish. The Fermi level is set at the top of the highest occupied positive energy state, and the negative energy states are ignored.

The no-pair approximation leads to a natural and straightforward extension of the nonrelativistic open shell CC theory. The multireference valence-universal Fock space coupled-cluster approach is employed here, which defines and calculates an effective Hamiltonian in a low-dimensional model (or P) space, with eigenvalues approximating some desirable eigenvalues of the physical Hamiltonian. According to Lindgren's formulation of the open-shell CC method [15], the effective Hamiltonian has the form

$$H_{\text{eff}} = PH\Omega P, \qquad \Omega = \{\exp(S)\}, \tag{4}$$

where Ω is the normal-ordered wave operator, and the excitation operator S is defined with respect to a closed-shell reference determinant. In addition to the traditional decomposition into terms with different total (l) number of excited electrons, S is partitioned according to the number of valence holes (m) and valence particles (n) to be excited with respect to the reference determinant,

$$S = \sum_{m\geq 0}\sum_{n\geq 0}\left(\sum_{l\geq m+n} S_l^{(m,n)}\right). \tag{5}$$

In the present application we use the $(m,n) = (0,0)$, (0,1), and (0,2) sectors. The lower index l is truncated at $l = 2$. The resulting coupled-clusters-singles-and-doubles (CCSD) scheme involves the fully self-consistent, iterative calculation of all one- and two-body virtual excitation amplitudes and sums all diagrams with these excitations to infinite order. Here we start by solving the Dirac-Fock-Coulomb (DFC) or Dirac-Fock-Breit (DFB) equations for the closed-shell system Rf^{+2} in the $[\text{Rn}]5f^{14}7s^2$ configuration, which defines the (0,0) sector. The ion is then correlated by CCSD, and two electrons are added, one at a time, in the $6d$ and $7p$ shells, recorrelating the system at each stage. Adding one electron gives the $6d7s^2$ and $7s^27p$ states of Rf^+, and addition of the second electron leads to the $6d^27s^2$, $6d7s^27p$, and $7s^27p^2$ states of the neutral atom. In addition to the valence $6d$ and $7p$ electrons, we correlated the $5d$, $5f$, $6s$, $6p$, and $7s$ shells, so that only the 68 electrons of $[\text{Xe}]4f^{14}$ were treated as core. To avoid "variational collapse" [16,17], the Gaussian spinors in the basis are made to satisfy kinetic balance [18]. They also satisfy relativistic boundary conditions associated with a finite nucleus, described here as a sphere of uniform proton charge [14]. We used an atomic mass of 261.1, and the speed of light c was set at 137.035 99 a.u.

The universal basis set of Malli, Da Silva, and Ishikawa [19] is used. It consists of Gaussian-type orbitals, with exponents given by the geometric series

$$\zeta_n = \alpha\beta^{(n-1)}, \qquad \alpha = 106\,111\,395.371\,615, \\ \beta = 0.486\,752\,256\,286. \tag{6}$$

The largest basis included 34 s functions ($n = 1-34$), 24 p ($n = 9-32$), 19 d ($n = 13-31$), 13 f ($n = 17-29$), 8 g ($n = 21-28$), 5 h ($n = 24-28$), and 4 i orbitals ($n = 25-28$). The orbitals were left uncontracted. Virtual orbitals with energies higher than 80 hartrees were omitted. A series of calculations with high-l orbitals deleted was performed, to study convergence with respect to the basis and make possible the comparison with the MCDF results [3,4], which did not include high-l functions.

The correlation energy of Rf^{+2} in the different basis sets as well as energies of adding one or two electrons and the total energy of Rf are given in Table I. Large correlation effects are observed for the $5f$ electrons and for virtual orbitals with l up to 6. The energies of adding the electrons (essentially the ionization potentials of Rf^+ and Rf) show reasonable convergence, with the

TABLE I. Correlation energy of the Rf^{+2} ground state, energies of the Rf^+ $6d_{3/2}7s^2\ {}^2D_{3/2}$ and Rf $6d_{3/2}^27s^2\ {}^3F_2$ states relative to Rf^{+2}, and total energies of Rf ${}^3F_2$. All energies in hartrees, signs reversed. The DFC energy of Rf^{+2} is −38 684.554 829 hartrees, its DFB energy is −38 591.133 718 hartrees.

Basis for correlation	E_{corr} Rf^{+2}	ΔE Rf^+	ΔE Rf	Total E Rf
$34s24p19d$[a]	0.261 536	0.491 469	0.680 605	38 685.496 96
$34s24p19d13f$[a]	0.333 455	0.512 565	0.720 071	38 685.608 35
$34s24p19d13f$	0.793 010	0.516 238	0.727 985	38 686.075 82
$34s24p19d13f8g$	1.561 428	0.521 890	0.738 558	38 686.854 81
$34s24p19d13f8g5h$	1.782 960	0.526 817	0.746 796	38 687.084 58
$34s24p19d13f8g5h4i$	1.856 642	0.527 917	0.748 783	38 687.160 25
$34s24p19d13f8g5h$[b]	1.784 356	0.526 863	0.747 027	38 593.665 09

[a] $5f$ electrons not correlated.

[b] With Breit interaction included.

TABLE II. Ionization potentials (IP) and excitation energies (EE) of Rf^+ and Rf (eV). $5df6spd7sp$ electrons correlated, unless otherwise noted.

			CCSD, with virtual orbitals up to l =						
	State	MCDF[a]	2[b]	3[b]	3	4	5	6	5[c]
				Rf^+					
IP	$7s^2 6d_{3/2}\,{}^2D_{3/2}$	13.47	13.374	13.948	14.048	14.201	14.335	14.365	14.337
EE	$7s^2 6d_{5/2}\,{}^2D_{5/2}$		0.791	0.815	0.870	0.904	0.920	0.923	0.909
	$7s^2 7p_{1/2}\,{}^2P_{1/2}$		1.564	2.053	2.145	2.268	2.382	2.404	2.407
	$7s^2 7p_{3/2}\,{}^2P_{3/2}$		3.475	4.005	4.116	4.252	4.379	4.403	4.387
				Rf					
IP	$7s^2 6d\ {}^3F_2$	5.30	5.147	5.646	5.762	5.896	5.986	6.010	5.991
EE	$7s^2 7p6d\,{}^3D_2$	−0.24	−0.602	−0.108	0.033	0.166	0.254	0.274	0.274
	$7s^2 6d\ {}^3F_3$		0.520	0.534	0.577	0.598	0.611	0.613	0.602
	${}^3P_0$		0.384	0.500	0.570	0.642	0.650	0.651	0.655
	${}^3P_2$		0.692	0.777	0.861	0.926	0.943	0.948	0.935
	${}^3F_4$		0.932	0.939	1.010	0.986	1.050	1.053	1.038
	$7s^2 7p6d\,{}^3D_1$		0.338	0.763	0.877	1.037	1.069	1.081	1.086
	$7s^2 6d^2\,{}^3P_1$		0.798	0.869	0.980	1.062	1.067	1.074	1.088
	$7s^2 7p6d\,{}^1D_2$		0.389	0.899	1.078	1.239	1.342	1.366	1.352
	${}^3D_3$		0.629	1.085	1.239	1.372	1.467	1.489	1.476

[a] Ref. [4].

[b] $5f$ electrons not correlated.

[c] Breit interacton included.

i ($l = 6$) orbitals changing IPs by 1 millihartree. The Breit interaction has a large effect on total energies, but a very small effect on correlation and transition energies in the outer shells. Table II shows the CCSD ionization potentials and lowest excitation energies, and compares them with available MCDF results. Higher excitation energies were also calculated, but are not listed. The transition energies show monotonic increase with the maximum l of virtual orbitals, and seem to converge to a few hundredths of an eV. The MCDF results generally fall between the first two CCSD columns in Table II, which correspond to d and f limits without correlating the $5f$ electrons. This is very reasonable, since MCDF includes only the nondynamic correlation of the outer four electrons. The effect of the Breit interaction on transition energies is small, on the order of 10^{-2} eV.

The quantity of main interest is the energy difference between the $7s^2 6d^2\,{}^3F_2$ and $7s^2 7p6d\,{}^3D_2$ levels of Rf. MCDF calculations predict the latter to be lower by 0.24–0.5 eV. CCSD calculations freezing the $5f$ electrons and going only to $l \leq 3$ in the virtual space give similar results. However, as the amount of dynamic correlation included in the calculation increases, the order is reversed, and the $6d^2$ level becomes more and more stabilized. *We therefore conclude that the ground state of Rf is* $[\mathrm{Rn}]5f^{14}6d^2 7s^2\,{}^3F_2$. This state is analogous to that of lighter group 4 elements, although the excitation energy to the $6d7p\,{}^3D_2$ state is much lower for Rf, due to relativistic effects. Extrapolating the results of Table II, and including the Breit contribution of 0.02 eV, we estimate the CCSD limit of this excitation energy at 0.30–0.31 eV. The error in the MCDF results is thus similar to errors found in differences between $(n - 1)d$ and np levels in other systems [6]. The best CCSD ionization potential of the atom is 6.01 eV, 0.70 eV higher than the MCDF estimate. Dynamic correlation may play an important role in determining level order in other heavy elements.

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