

Ground State Electron Configuration of Element 111

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The low-lying electronic states of element 111 are investigated by the relativistic coupled-cluster method based on the Dirac-Coulomb-Breit Hamiltonian. A large basis set (26s21p16d9f7g5h) of Gaussian-type orbitals is used. In contrast to the lighter group 11 elements, the ground state of the atom is $6d^9 7s^2 {}^2D_{5/2}$; the ${}^2D_{3/2}$ state is higher by 2.69 eV, and the $6d^{10} 7s^2 S$ lies 2.95 eV above the ${}^2D_{5/2}$. The reversal is ascribed to relativistic effects; without them, the 2S energy is 5.43 eV below the 2D . The calculated electron affinity of the atom is 1.56 eV, and its ionization potential is 10.6 eV.

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The gold atom represents a local maximum in the size of relativistic effects [1]. One manifestation of these effects involves the energy separation between the $5d^{10} 6s^2 S$ ground state and the $5d^9 6s^2 {}^2D$ excited state. Looking at the group 11 (or coinage metal) atoms, the 2D excitation energies of Cu are 1.389 ($J = 5/2$) and 1.642 ($J = 3/2$) eV, increasing to 3.749 and 4.304 eV for Ag [2]. Were it not for relativity, one would expect even higher energies for Au. Indeed, recent high-precision calculations using the coupled-cluster method with single and double excitations (CCSD) [3] put the nonrelativistic 2D energy at 5.301 eV above the 2S ground state, in line with expectations. Relativistic effects change this value radically, giving 1.150 and 2.658 eV for the excited 2D sublevels [3]. These energies are within 0.015 eV of experiment [2]. Qualitatively, the stabilization of s relative to d orbitals in the $5d$ elements has been predicted before, e.g., by quasirelativistic Hartree-Fock calculations [4].

The dramatic reduction of the 2D excitation energies in Au suggests an even larger effect for the next group 11 element, with atomic number 111. A large enough reduction would bring the 2D state below the 2S , leading to a $d^9 s^2$ ground state configuration of the atom, rather than the $d^{10} s$ of the other coinage metals. This reduction has, in fact, been predicted by means of Hartree-Fock-Slater (HFS) calculations [5], and ionization potential and electron affinity have been obtained using Koopmans' theorem as well as by the difference of HFS energies in order to derive the stabilities of the various oxidation states, and thus information about the expected chemistry of element 111. It should be noted that the reported HFS ionization potentials of Au are 0.5–1 eV in error.

The early HFS studies on superheavy elements have been reviewed by Fricke [6].

The relativistic Fock-space CCSD method is, of course, much more accurate, taking into account simultaneously relativistic and correlation effects to high orders. It has recently proved highly successful for transition energies in Au [3]. It is therefore eminently suitable for accurate calculation of the $6d^9 7s^2 {}^2D - 6d^{10} 7s^2 S$ energy difference in element 111, and hence its ground state electron configuration.

The relativistic coupled-cluster method has been applied to the Au atom [3], to highly ionized atoms with 2–5 electrons [7], to the alkali metal atoms up to Fr [8], and to f^2 excitations in Pr^{+3} and U^{+4} [9]. A detailed description of the method may be found in these papers. We start from the projected Dirac-Coulomb (DC) or Dirac-Coulomb-Breit (DCB) Hamiltonian [10,11]

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

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 Coulomb gauge, correct to second order in the fine-structure constant α , is the

Coulomb-Breit potential [12]

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

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 $\{r^+s^+ut\}$ [10,13],

$$H = H_+ - \langle 0|H_+|0\rangle = \sum_{rs} f_{rs} \{r^+s\} + \frac{1}{4} \sum_{rstu} \langle rs||tu\rangle \{r^+s^+ut\}, \quad (3)$$

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 [14], the effective Hamiltonian has the form

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

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,

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

In the present application we use the $(m,n) = (0,0)$, $(1,0)$, and $(2,0)$ sectors. The lower index l is truncated at $l = 2$. The resulting 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 111^- in the $6d^{10}7s^2$ configuration, which defines the $(0,0)$ sector. The anion is then correlated by CCSD, and up to two electrons are removed from the $6d$ and $7s$ shells, recorelating the system at each stage. Removing one electron gives the 2D and 2S states of the neutral 111 , and ionization of the second electron leads to the d^{10} , d^9s , and d^8s^2 states of the positive ion. To avoid "variational collapse" [15,16], the Gaussian spinors in the basis are made to satisfy kinetic balance [17]. They also satisfy relativistic boundary conditions associated with a finite nucleus, described here as a sphere of uniform proton charge [13]. We used an atomic mass of 269, and the speed of light c was set at 137.03599 atomic units. Nonrelativistic results were obtained with $c = 10^5$ a.u.

The basis set used was optimized using the procedure described in [18] and is given in Table I. It consists of $(26s21p16d9f7g5h)$ Gaussian-type orbitals, without contraction. Atomic orbitals with the same l but different k number (e.g., $p_{1/2}$ and $p_{3/2}$) are expanded in the same basis functions. The quality of the basis may be judged by comparing numerical DFC orbital energies [19] with those obtained using the basis. Such a comparison is provided in Table II for the uniformly charged finite nucleus, showing good agreement between numerical and basis-set energies. Replacing the finite nucleus by a point nucleus has a much larger effect on orbital energies.

TABLE I. Basis set.

l	Exponents of Gaussian-type orbitals
s	62 403 300, 11 747 900, 2 975 270, 876 539, 272 668, 90 117.7, 33 080.1, 13 358.9, 5715.77, 2535.25, 1150.6, 439.73, 207.222, 79.6407, 44.6981, 15.8297, 8.355 88, 3.634 78, 1.58, 0.687, 0.298, 0.130, 0.056, 0.0243, 0.0105, 0.004 58
p	757 984, 250 978, 79 190.9, 23 508.5, 8302.39, 3336.07, 1448.41, 658.028, 308.248, 143.799, 70.8851, 33.7763, 16.9894, 7.399 31, 3.655 11, 1.83, 0.914, 0.457, 0.228, 0.113 75, 0.056 75
d	4489.33, 1301.84, 495.293, 215.213, 100.527, 48.2317, 23.488, 11.4891, 5.420 16, 2.56, 1.21, 0.569, 0.268, 0.127, 0.060 183, 0.028 552
f	679.352, 229.026, 95.415, 43.2829, 20.2221, 9.146 51, 4.14, 1.87, 0.847
g	2.56, 1.21, 0.569, 0.268, 0.127, 0.060 183, 0.028 552
h	1.21, 0.569, 0.268, 0.127, 0.060 183

TABLE II. Orbital energies of the 111 anion. Numerical DFC with point and uniformly charged nucleus compared with basis-set uniformly charged nucleus in the DFC, DFB, and nonrelativistic HF approximations (a.u., signs reversed).

Orbital	Numerical DFC		Basis set, uniform nucleus		
	Point	Uniform	DFC	DFB	HF
6s	5.0668	5.0102	5.0071	4.9933	3.0831
7s	0.1439	0.1372	0.1367	0.1356	0.0181
6p _{1/2}	3.5158	3.5091	3.4887	3.4674	2.0249
6p _{3/2}	1.9338	1.9390	1.9396	1.9346	2.0249
6d _{3/2}	0.1830	0.1863	0.1863	0.1860	0.3550
6d _{5/2}	0.0761	0.0790	0.0789	0.0800	0.3550
5f _{5/2}	2.6698	2.6769	2.6778	2.6842	3.4884
5f _{7/2}	2.4451	2.4519	2.4530	2.4644	3.4884

The DFC, DFB, and nonrelativistic Hartree-Fock (HF) energies of the high occupied orbitals of 111⁻ are given in Table II. Relativity has a very large effect on orbital energies. Of particular interest to us is the considerable lowering of the 7s orbital, accompanied by raising the 6d, particularly the 6d_{5/2}. While the nonrelativistic 7s lies 0.34 hartree above the 6d, the order is reversed in the relativistic approach, with the 6d 0.055 hartree above the 7s, pointing to the likelihood of a 6d⁹7s² ground state configuration for the neutral atom. Other orbitals are also affected. The large spin-orbit splitting of the 6p and 6d orbitals should be noted. Another noteworthy effect is the very large relativistic contraction of the 7s orbital. The relativistic and nonrelativistic 7s electron densities calculated for the 6d⁹7s² configuration are shown in Fig. 1.

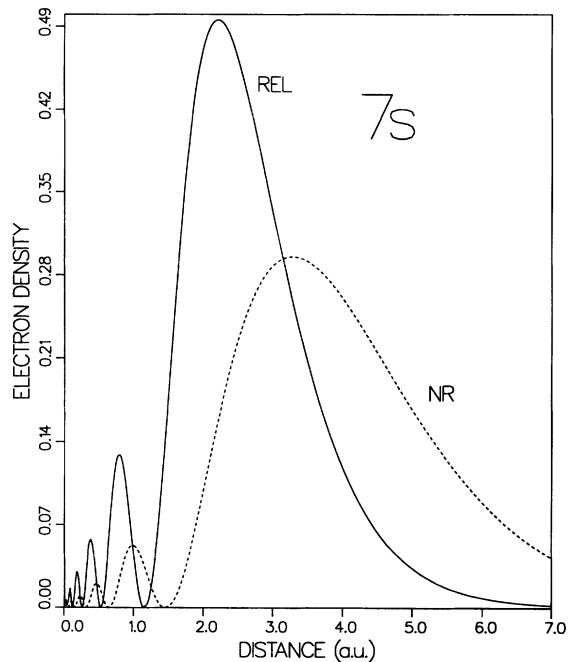


FIG. 1. Electron density of the relativistic (solid line) and nonrelativistic (dashed) 7s orbital, calculated in the 6d⁹7s² configuration.

Inclusion of the Breit interaction has small effect on the orbitals or their energies.

Next, correlation is included by the CCSD method described above. The 5f6spd7s shells are correlated. Virtual orbitals with high orbital energies have been found to contribute very little to correlation effects on transition energies; orbitals higher than 40 a.u. are therefore eliminated from the coupled-cluster calculation, effecting considerable savings in computational effort. The resulting excitation energies (EE), electron affinity (EA), and a few of the ionization potentials (IP) are shown in Table III. The 6d⁹7s²D_{5/2} state is about 3 eV below the 6d¹⁰7s²S. The accuracy of the results may be estimated by comparison with our previous calculations for Au [3]. Errors in the corresponding Au EEs were 0.015 eV or less; the EA was correct to 0.04 eV, while somewhat larger errors (0.1–0.2 eV) were found for the IPs. The present calculation should have roughly the same accuracy. We therefore conclude that the ground state of element 111 is definitely 6d⁹7s²D_{5/2}. The IPs collected in Table III are those leading to the lowest state of each of the 6d⁸7s², 6d⁹7s, and 6d¹⁰ configurations. Obviously, the order of the three configurations is reversed relative to Au⁺, and the ground state of the 111 cation is 6d⁸7s². It is interesting to note that the HFS results [5] were not very far from ours. Thus, they predicted a ²S-²D_{5/2} separation of 2.9 eV (we get 3.0 eV), an EA of 1–1.3 eV (vs 1.55 eV), and their IP was 10.14 eV (vs our 10.60 eV).

In summary, very large relativistic effects on orbital energies and level order of element 111 are observed. In particular, the 6d orbital goes well above the 7s. Contrary to the lighter coinage metals, with d¹⁰s ground configurations, the lowest state of 111 is 6d⁹7s². The ground state of the cation is 6d⁸7s². The excitation energies and electron affinity are expected to be accurate to a few hundredths of an eV, and the ionization potentials to 0.1–0.2 eV.

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TABLE III. CCSD excitation energies (EE), electron affinity (EA), and ionization potentials (IP) of element 111 (eV).

	Transition	DC	DCB	NR
EE	6d ⁹ 7s ² 2D _{5/2} → 6d ⁹ 7s ² 2D _{3/2}	2.719	2.687	0
	6d ⁹ 7s ² 2D _{5/2} → 6d ¹⁰ 7s ² S _{1/2}	3.006	2.953	-5.430
EA	6d ⁹ 7s ² 2D _{5/2} → 6d ¹⁰ 7s ² 1S ₀	1.542	1.565	6.484
IP	6d ⁹ 7s ² 2D _{5/2} → 6d ⁸ 7s ² 3D ₄	10.57	10.60	22.98
	6d ⁹ 7s ² 2D _{5/2} → 6d ⁹ 7s ³ D ₃	12.36	12.33	0.92
	6d ⁹ 7s ² 2D _{5/2} → 6d ¹⁰ 1S ₀	15.30	15.23	-0.44

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