Element 118: The First Rare Gas with an Electron Affinity

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The electron affinity of the rare gas element 118 is calculated by the relativistic coupled cluster method based on the Dirac-Coulomb-Breit Hamiltonian. A large basis set ($34s26p20d14f9g6h4i$) of Gaussian-type orbitals is used. The external 40 electrons are correlated. Inclusion of both relativity and correlation yields an electron affinity of 0.056 eV, with an estimated error of 0.01 eV. Nonrelativistic or uncorrelated calculations give no electron affinity for the atom. [S0031-9007(96)02040-6]

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Studies of superheavy elements have been partially motivated by the hope of finding exotic, unexpected electronic properties, due to the relativistic effects, such as the stabilization of s shells or the destabilization of high-l (d and f) shells. We have earlier shown that the ground-state $d^{10}s^1$ electron configuration of the lighter coinage metals (Cu, Ag, Au) is replaced by d^9s^2 for ekagold, element 111 [1], and that analogous changes occur for ekamercury, element 112 [2]. Even the next element, the main-group ekathallium E113, has a chance of behaving as a transition metal [3].

Not only the occupied but also the initially empty s levels are stabilized by relativity. As an example, the yellow color of PbCl_6^{2-} was attributed to the relativistic stabilization of the low-lying, empty a_1 molecular orbital [4]. We now consider the possibility that the stabilization of the $8s$ shell would be large enough to give an electron affinity to ekaradon, element 118. The first known case of a closed-shell atom with an electron affinity was that of Ca [5–7]. The added electron there had the same principal quantum number as the valence electrons, with the configuration ns^2np. Here we consider adding an electron with a higher principal quantum number, yielding a $ns^2np^6(n+1)s$ configuration. Long-lived Xe^- has been reported [8], but no state assignments were made, and it was not determined whether the observation corresponded to a bound state or a resonance. Calculations by Nicolaides and Aspromallis [9] found no bound state of Xe^-.

The method we employ is relativistic coupled cluster (RCC) with single and double excitations. This method has been applied to a series of heavy elements, including Au [10], Pr^{3+} and U^{4+} [11], Yb and Lu [12], Hg [2], Tl [3], and Ra [13], as well as the superheavy elements Lr [12], 104 [14], 111 [1], 112 [2], and 113 [3]. The properties calculated are primarily transition energies, including ionization potentials, excitation energies, and electron affinities. Good agreement with experimental values is obtained when the latter are known; in other cases predictions may be made regarding order and separation of electronic states.

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 [10,11], and only a brief account is given here. We start from the projected Dirac-Coulomb (DC) or Dirac-Coulomb-Breit (DCB) Hamiltonian [15–18]

$$H_+ = \Lambda^+ \Big[\sum_i [c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_{\mathrm{nuc}}(i)] + \sum_{i<j} V(i,j) \Big] \Lambda^+ . \qquad (1)$$

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 two-electron potential in Coulomb gauge, correct to second order in the fine-structure constant α, is the Coulomb-Breit potential [16,17,19]

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

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

Using the second quantization formalism, the DCB Hamiltonian H_+ is rewritten in terms of normal-ordered products of the spinor operators, $\{r^+s\}$ and $\{r^+s^+ut\}$

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[17,20]

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

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 [21], the effective Hamiltonian has the form

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

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 $(m,n) = (0,0)$ and (0,1) 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 all-electron Dirac-Fock-Coulomb (DFC) or Dirac-Fock-Breit (DFB) equations for the closed-shell neutral E118 atom, which defines the (0,0) sector. This state is correlated by CCSD; an electron is then added in the $8s$ orbital, recorrelating the whole system. The correlated orbitals include the $5f$, $6spd$, and $7sp$ shells, 40 electrons in all; the 78 electrons of $[\mathrm{Xe}]4f^{14}5d^{10}$ are treated as the core. To avoid "variational collapse" [22,23], the Gaussian spinors in the basis are made to satisfy kinetic balance [24]. They also satisfy relativistic boundary conditions associated with a finite nucleus, described here as a sphere of uniform proton charge [20]. We use an atomic mass of 302, and the speed of light c is set at 137.035 99 atomic units.

The universal basis set of Malli *et al.* [25] is employed. It consists of Gaussian-type orbitals, with exponents given by the geometric series

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

The largest basis included 34 s functions ($n = 1$–34), 26 p ($n = 9$–34), 20 d ($n = 13$–32), 14 f ($n = 17$–30), 9 g ($n = 21$–29), 6 h ($n = 24$–29), and 4 i orbitals ($n = 25$–28). The orbitals were left uncontracted. Virtual orbitals with energies higher than 80 hartree were omitted.

The RCC calculation gave an electron affinity (EA) of 512 cm^{-1}, or 0.063 eV. The Breit interaction has a negligible effect, changing the EA by 3 cm^{-1}. Nonrelativistic CC yields no electron affinity. The orbital energy of the $8s$ Dirac-Fock orbital is positive, so that the Koopmans' EA is also negative. This causes the (unbound) orbital to "escape" to the most diffuse functions available in the basis and raises the question of its suitability as a starting point for the RCC EA calculation. To study this question a series of tests were carried out, where the unoccupied orbitals were computed in different electronic fields, obtained by assigning partial charges to some of the external shells, thus leading to a bound $8s$ orbital. These artificial fields were compensated by appropriate correction of the perturbation term. Assigning a charge of $0.8e$ to the $7p_{3/2}$ electrons gave an EA of 454 cm^{-1}; a charge of $0.75e$ on the $7s$ electrons yielded 449 cm^{-1}; and putting $0.9e$ on all $7s$ and $7p$ electrons yielded an electron affinity of 437 cm^{-1}. These results are quite close to each other and not too far from the 512 cm^{-1} quoted above; we regard them as more reliable than the latter.

Several other tests were performed, all with a charge of $0.8e$ on the $7p_{3/2}$ electrons, to estimate the stability and reliability of the calculated EA. To check the dependence on the nuclear mass A, it was changed from 302 to 283; the effect on the EA was only 3 cm^{-1}. A larger difference, with an EA of 618 cm^{-1}, was obtained with a point nucleus; this is, however, not a very realistic model for such a heavy atom. Finally, to assess the basis set convergence, the f, g, and h limits of the EA were calculated; they came out as 427, 447, and 452 cm^{-1}, respectively. The convergence is satisfactory. Our value for the electron affinity of element 118 is 0.056 eV. The estimated error bounds are about 0.01 eV. Similar calculations gave no $2S$ bound state for Rn^-.

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