

Electron affinity of Ce and electronic states of Ce⁻

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Relativistic energy-consistent small-core lanthanide pseudopotential multireference configuration-interaction (MRCI) studies yield 15 bound states for Ce⁻. These include twelve bound states with 5*d* attachment with the following electron affinities (in meV with corresponding *J* in parentheses): 530 (7/2), 421 (9/2), 332 (7/2), 276 (9/2), 242 (9/2), 229 (11/2), 168 (5/2), 101 (11/2), 96 (7/2), 84 (13/2), 62 (3/2), 18 (5/2). The remaining three bound states result from 6*p* attachment with the following electron affinities: 156 (9/2), 80 (5/2), 8 (7/2). Considering averaged coupled pair functional-type corrections to the MRCI value as well as possible finite basis set errors the final relativistic result for the electron affinity of Ce is 0.58±0.1 eV. The present results are compared to experimental measurements, as well as to data from other theoretical calculations.

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I. INTRODUCTION

In 2002 Davis *et al.* [1] measured the EA (electron affinity) of cerium Ce(¹G₄) using laser photodetachment electron spectroscopy. The determined EA of 0.955±0.026 eV [1] strongly disagrees with the most recent theoretical result (0.428 eV) [2] obtained from valence shell relativistic configuration interaction calculations, and is much larger than the previous experimental results (≥0.5 eV [3], 0.7 eV [4]). The significant disagreement highlights the complicated nature of the electronic structure of this particular lanthanide element. From the experimental point of view the present experimental sensitivity is insufficient to determine the existence of excited bound states of Ce⁻. From the theoretical point of view the presence of several open shells with different main quantum numbers brings about large difficulties in accounting precisely for electron correlation contributions.

Semiempirical estimates of the EA of certain lanthanides have been made in the past [5–7]. A more recent *ab initio* calculation of Ce and Ce⁻ by O'Malley and Beck [2,8] was based on the valence shell relativistic configuration-interaction (CI) method which begins by generating either Dirac-Fock (DF) or multiconfigurational Dirac-Fock (MCDF) many-electron reference functions and then increases the CI space by adding systematically excitations in virtual orbitals until the underlying one-electron basis is radially saturated. Single and double excitations from the outer valence orbitals 5*d*, 6*s*, and 6*p* were accounted for, whereas the inner valence orbital 4*f* was kept singly occupied throughout the calculations. The ground-state configuration for Ce⁻ was initially predicted as 4*f*¹5*d*¹6*s*²6*p*¹ *J*=9/2 (6*p* attachment) [8], however, later an improved calculation (including also some triple and quadruple excitations) by the same authors showed that the possible ground state might be 4*f*¹5*d*²6*s*² *J*=7/2 (5*d* attachment) [2].

Recently, we published energy-optimized (14*s*13*p*10*d*8*f*6*g*)/[6*s*6*p*5*d*4*f*3*g*] atomic natural orbital

Gaussian valence basis sets for the whole lanthanide series [9]. Excellent agreement with experimental data was obtained for lanthanide ionization potentials, i.e., mean absolute (relative) errors of less than 0.3 eV (4%) were obtained for IP₁ and IP₂, whereas for IP₃ and IP₄ they amount up to 0.6 eV (2%) [9]. Calculations with the extended basis sets [uncontracted (14*s*13*p*10*d*8*f*6*g*) basis sets augmented by a diffuse (2*s*2*p*2*d*2*f*2*g*) set as well as (8*h*) and (8*i*) sets] and basis set limit extrapolation techniques reproduced IP₃ and IP₄ with an accuracy of 0.34 eV (1%) [10]. Recent resurgence of experimental interest in Ce⁻, as well as our recent work, has encouraged us to investigate the rare-earth negative ion Ce⁻. In this paper, a relativistic energy-consistent small-core cerium pseudopotential of the Stuttgart-Köln variety [11] and extended valence basis sets [9] have been used for the investigation of the Ce EA and bound states of Ce⁻. Spin-orbit matrix elements and eigenstates were computed using corresponding spin-orbit pseudopotentials.

II. COMPUTATIONAL METHODS

The relativistic energy-consistent small-core pseudopotential used here for cerium [9,11] is applied in the following valence-only model Hamiltonian for an atom or ion with *n* valence electrons:

$$H_v = -\frac{1}{2} \sum_i^n \Delta_i + \sum_{i<j}^n \frac{1}{r_{ij}} + V_{av} + V_{so}.$$

Here *i* and *j* are electron indices. *V*_{av} stands for a (spin-orbit averaged) scalar-relativistic pseudopotential in a semilocal form for a core with charge *Q*

$$V_{av} = -\sum_i^n \frac{Q}{r_i} + \sum_i^n \sum_{l,k} A_{lk} \exp(-a_{lk} r_i^2) P_l.$$

The Ce 1*s*-3*d* shells are included in the pseudopotential core (small-core pseudopotential), while all shells with main quantum number larger than 3 are treated explicitly (*Q* = 30). *P*₁ is the projection operator onto the Hilbert subspace

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of angular momentum l . V_{so} is a corresponding spin-orbit term

$$V_{so} = \sum_i^n \sum_{l>0,k} \frac{2}{2l+1} B_{lk} \exp(-b_{lk}r_i^2) P_{l_i} s_i P_l.$$

The free parameters A_{lk} , a_{lk} , B_{lk} , and b_{lk} are adjusted to reproduce *ab initio* relativistic all-electron valence total energies of a multitude of low-lying electronic states of the neutral atom and its ions, i.e., only quantum-mechanical observables like (sums of) ionization potentials and excitation energies are used as reference data. Recently developed Gaussian (14s13p10d8f6g) atomic valence basis sets augmented by a diffuse (2s2p2d2f2g) set as well as (8h) and (8i) sets were applied [9]. The g , h , and i exponents were chosen to be identical to the f exponents with the largest expansion coefficients in the $4f$ orbital. All calculations were performed with the MOLPRO *ab initio* electronic structure program [12–15].

Many low-lying states of Ce^- formed by $6p$, $5d$, and $4f$ attachment were studied. The complete active space self-consistent field (CASSCF) method [16] was used to generate the orbitals for the subsequent multireference configuration interaction (MRCI) and the approximately size-extensive multireference averaged coupled-pair functional (ACPF) calculations [17]. The non-size-extensive MRCI results were corrected approximately using the Siegbahn cluster correction (MRCI+Q) [18]. We note that ACPF takes into account the approximate corrections of higher-order excitations iteratively (self-consistently), whereas the Siegbahn correction is applied to the converged MRCI result, i.e., ACPF should be superior to MRCI+Q.

The CASSCF variant of the multiconfiguration self-consistent field method allows for a simultaneous optimization of the orbitals and configuration interaction coefficients. The CASSCF wave function corresponds to a full CI in a given orbital set (active space). For Ce and Ce^- we chose the $4f$, $5d$, and $6s$ orbitals to be active. For $6p$ attachment $6p$ was also included in the active space. The $4s$, $4p$, $4d$, $5s$, $5p$ orbitals were kept doubly occupied. Due to the limits of our current hardware capabilities, the MRCI (ACPF) configuration space was obtained by single and double excitations with respect to the CASSCF reference wave function with a selection threshold 0.01 which applies to the norm of all configuration state functions for each orbital configuration, i.e., singly and doubly excited configurations were only generated from those configuration state functions which contribute more than 1% to the CASSCF references. The $4s$, $4p$, $4d$ orbitals were frozen in the MRCI and ACPF calculations unless otherwise noted. In order to get a correct state average in CASSCF calculations for the configuration $4f^2 5d^1 6s^2$ and the quartet states of the configuration $4f^1 5d^1 6s^2 6p^1$, the occupation numbers of electrons for the $4f$, $6p$, $5d$, and $6s$ orbitals were restricted to 2, 0, 1, 2, and 1, 1, 1, 2, respectively. The MRCI+Q energy without occupation restriction for the quartet states of $4f^1 5d^1 6s^2 6p^1$ (4G , 4F), which are required for subsequent spin-orbit calculations, were estimated by taking into account the averaged energy differences for

doublet states of the $6p$ attachment ($4f^1 5d^1 6s^2 6p^1$, 2G , 2H , 2F) with and without restrictions.

The dynamical correlation energies $E(l)$ obtained from calculations with basis sets up to $g(l=4)$, $h(l=5)$, and $i(l=6)$ functions were found to be almost linear in $1/l^3$, when l denotes the maximum angular quantum number in the basis set. The correlation coefficient was found to deviate by less than 10^{-4} from the ideal value of one for all cases. The extrapolations $1/l^3 \rightarrow 0$ yield the basis set limit $E(\infty)$ for the dynamical correlation energies.

$$E(l) = al^{-3} + E(\infty).$$

Spin-orbit-coupling calculations were done using spin-orbit pseudopotentials [11]. Many low-lying states of Ce^- formed by $6p$ and $5d$ attachment were included, i.e., $4f^1 5d^2 6s^2$: 4H , 4I , 4D , 2G , 2F , 2S , 2H , 2I ; $4f^1 5d^1 6s^2 6p^1$: 4G , 4F , 2G , 2H , 2F . The state-interacting method was employed, which means that the spin-orbit eigenstates are obtained by diagonalizing $\mathbf{H}_{el} + \mathbf{H}_{SO}$ in a basis of eigenfunctions of \mathbf{H}_{el} . Since often it is sufficient to compute the spin-orbit matrix elements in a smaller basis or at lower computational level than the diagonal scalar-relativistic energies, a contracted (14s13p10d8f6g)/[6s6p5d4f3g] basis set [9] was used to compute the spin-orbit matrix elements at the CASSCF level, and the energy eigenvalues were replaced by the MRCI+Q energies at the basis set limit.

The EA was calculated with respect to the neutral Ce atom in the $4f^1 5d^1 6s^2$ 1G_4 ground state. For spin-orbit-coupling calculations of Ce, the $4f^1 5d^1 6s^2$ 1G , 3F , and 3H states were included to calculate the energy of the ground state in the intermediate coupling scheme.

III. RESULTS

Ce has a $4f^1 5d^1 6s^2$ 1G_4 ground state. The open $4f$ and $5d$ shells and the unoccupied low-lying $6p$ shell make it very difficult to guess the ground state for Ce^- at first glance. Therefore many low-lying states of Ce^- corresponding to $5d$, $6p$, and $4f$ attachment to Ce were studied, cf. Table I. From the orbital energetic point of view the $4f$ shell is the preferable choice, i.e., the $4f$ orbital energy is much lower than the partially occupied or empty $5d$ and $6p$ orbitals, cf. Fig. 1. However, no bound states for Ce^- formed by $4f$ attachment were found (cf. Table I), i.e., the lowest $4f$ attached state Ce^- $4f^2 5d^1 6s^2$ 4K is roughly 1.6 eV higher than the Ce ground state 1G . It should be mentioned that the $4f$ shell is more compact than the diffuse $5d$, and especially $6p$ shells, cf. Fig. 2. Therefore the increase of the electron occupation in the $4f$ shell leads to a high electron-electron repulsion. Except for the $4f$ shell $5d$ is the energetically lowest orbital, which is not fully occupied. Several energetically close bound states for Ce^- formed by a $5d$ attachment are found, cf. Table I, e.g., the lowest doublet state 2G is only about 0.1 eV lower than the lowest quartet state 4H . Besides the $5d$ shell $6p$ is another host candidate for the additional electron, cf. Fig. 1. The lowest $6p$ attached state Ce^- $4f^1 5d^1 6s^2 6p^1$ 2G was found to be about 0.3 eV higher than lowest $5d$ attached state $4f^1 5d^2 6s^2$ 2G at the ACPF level, cf. Table I. It was found that ACPF calculations increase the EA of Ce by roughly 0.1 eV

TABLE I. Basis sets extrapolation results for the energies (in eV) of some low-lying states of Ce^- [the results from the standard uncontracted ($14s13p10d8f6g$) basis set augmented by a ($2s2p2d2f2g$) set are given in parentheses].

	MRCI	MRCI+Q	ACPF
$Ce^- f^1 d^2 s^2 {}^2G$	0	0	0
$Ce^- f^1 d^2 s^2 {}^4H$	0.066(0.074)	0.094(0.103)	0.076(0.095)
$Ce^- f^1 d^2 s^2 {}^2F$	0.242(0.246)	0.237(0.233)	(0.219)
$Ce^- f^1 d^1 s^2 p^1 {}^2G$	0.362(0.305)	0.400(0.248)	0.279(0.255)
$Ce^- f^1 d^1 s^2 p^1 {}^2H$	0.364(0.297)	0.409(0.332)	0.350(0.276)
$Ce^- f^1 d^2 s^2 {}^4I$	0.386(0.383)	0.360(0.354)	(0.171)
$Ce^- f^1 d^2 s^2 {}^4F$	0.416(0.411)	0.407(0.399)	(0.393)
$Ce^- f^1 d^1 s^2 p^1 {}^2F$	0.440(0.368)	0.459(0.376)	0.380(0.303)
$Ce^- f^1 d^1 s^2 p^1 {}^2D$	(0.475)	(0.488)	
$Ce^- f^1 d^2 s^2 {}^2S$	0.478(0.488)	0.391(0.458)	(0.355)
$Ce^- f^1 d^2 s^2 {}^4D$	0.509(0.501)	0.439(0.433)	(0.399)
$Ce^- f^1 d^2 s^2 {}^2H$	0.520(0.405)	0.508(0.389)	(0.450)
$Ce^- f^1 d^2 s^2 {}^4G$	0.522(0.514)	0.467(0.454)	(0.417)
$Ce^- f^1 d^2 s^1 p^1 {}^6I$	0.744(0.758)	0.840(0.853)	
${}^a Ce^- f^1 d^2 s^1 p^1 {}^4H$	0.806(815)	0.854(0.862)	
${}^a Ce^- f^1 d^1 s^2 p^1 {}^4G$	1.006(0.932)	0.898(0.801)	0.880(0.841)
${}^a Ce^- f^1 d^1 s^2 p^1 {}^4F$	1.065(0.991)	0.949(0.853)	
${}^a Ce^- f^2 d^1 s^2 {}^4K$	2.085(2.173)	2.069(2.155)	
${}^a Ce^- f^2 d^1 s^2 {}^2H$	2.011(2.110)	1.977(2.074)	

^aReferences configuration selection threshold 0.015, otherwise 0.01 (cf. text).

compared to the MRCI+Q results. Unfortunately, ACPF only works for a few states. Therefore the MRCI+Q results were transferred as scalar-relativistic energies into the spin-orbit calculations discussed below, and the EA of Ce at the ACPF level was estimated by adding an appropriate correction (0.1 eV) to the MRCI+Q values.

The full LS breakdown of the states obtained in the intermediate coupling scheme is provided in Table II ($5d$ attachment) and Table III ($6p$ attachment) along with the calculated EA's. The obtained lowest state of Ce^- ($4f^1 5d^2 6s^2 J=7/2$) is roughly 0.28 eV lower than the spin-orbit averaged ground state $4f^1 5d^2 6s^2 {}^2G$. The large lowering shows that spin-orbit coupling cannot be neglected. As a consequence of

spin-orbit coupling more bound states of Ce^- are obtained (Tables II and III), i.e., 15 bound states vs 8 bound states were obtained from spin-orbit and scalar calculations. The existence of many bound states for Ce^- proved by the present work agrees with the experimentally observed high yields of Ce^- [3]. Both quartet and singlet states make contributions to the same energy level J , e.g., for the Ce^- ground state $4f^1 5d^2 6s^2$ ($J=7/2$) 56% of the leading terms are from $4f^1 5d^2 6s^2 {}^4H$, 40% are from $4f^1 5d^2 6s^2 {}^2G$. To our knowl-

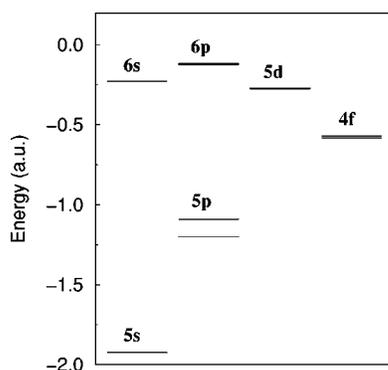


FIG. 1. Relativistic spinor energies for valence shells of Ce in the $4f^1 5d^1 6s^1 6p^1$ configuration from average level multiconfiguration Dirac-Hartree-Fock calculations [21].

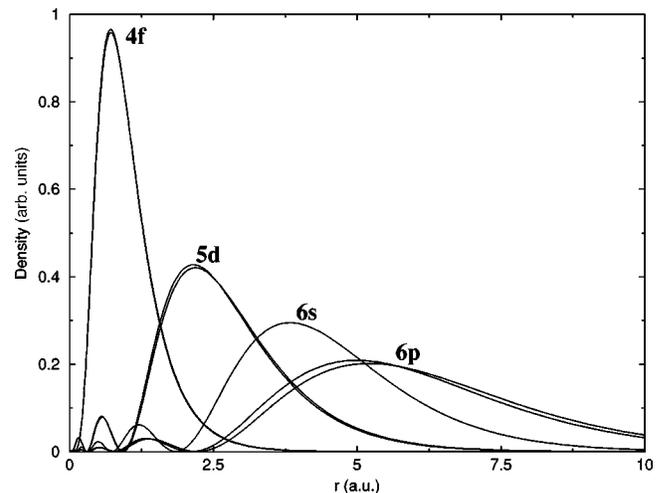


FIG. 2. Radial densities of the $4f$, $5d$, and $6s$ valence spinors of Ce in the $4f^1 5d^1 6s^1 6p^1$ configuration from average level multiconfiguration Dirac-Hartree-Fock calculations [21].

TABLE II. Electron affinities (in eV) and *LS* composition for Ce^- bound states with *5d* attachment.

<i>J</i> level (<i>LS</i> %)	EA (this work)	EA [2]
$7/2(^4H56.43, ^2G39.76, ^4F3.35, ^4G0.23, ^4F0.12, ^4D0.10)$	0.530	0.428
$9/2(^4H47.57, ^2G47.83, ^2H2.78, ^4F1, ^4I0.65, ^4G0.15)$	0.421	0.327
$7/2(^4H41.91, ^2G41.77, ^2F14.14, ^4G1.12, ^4D0.85, ^4F0.20)$	0.332	0.182
$9/2(^4H51.71, ^2G43.34, ^4I2.21, ^4F1.6, ^2H0.64, ^4G0.46)$	0.276	0.281
$9/2(^4I86.66, ^2H8.82, ^2G4.10, ^4F0.18, ^4G0.13, ^4H0.06)$	0.242	0.167
$11/2(^4H98.76, ^2H1.07, ^4G0.02, ^4I0.1)$	0.229	0.193
$5/2(^2F78.86, ^4G15.80, ^4D4.11, ^4F1.24)$	0.168	
$11/2(^4I95.93, ^2H3.74, ^4H0.26, ^4G0.02)$	0.101	0.149
$7/2(^2F62.63, ^2G15.40, ^4D14.17, ^4F4.97, ^4H1.55, ^4G1.26)$	0.0956	
$13/2(^4H99.96, ^4I0.01)$	0.0837	
$3/2(^4F99.92, ^4D0.10)$	0.0617	
$5/2(^4G52.07, ^4F41.61, ^2F4.42, ^4D1.89)$	0.0184	

edge there is no experimental information for the ground-state configuration of Ce^- .

However, O'Malley and Beck reported the same Ce^- ground state $4f^1 5d^2 6s^2$ ($J=7/2$) [2] using valence shell relativistic configuration-interaction calculations. The EA of Ce (0.530 eV) obtained at the MRCI+Q level is corrected to 0.63 eV at the ACPF level by adding the difference (ca. 0.1 eV) obtained from spin-orbit averaged calculations. The present theoretical value agrees well with the experimentally reported lower limit of 0.5 eV deduced from the relative yields of the negative ions by Nadeau *et al.* [3], as well as with the experimental value (0.70 eV) reported by Berkovits *et al.* [4] using a combination of laser excitation and AMS (accelerate mass spectroscopy). However it is still far below the newest experimental value (0.955 ± 0.026 eV) reported by Davis and Thompson [1] using laser photodetachment electron spectroscopy. In 1997 Nadeau *et al.* observed experimentally that La^- and Ce^- have relatively high yields compared to the other negative lanthanide ions. The same lower limit (≥ 0.5 eV) for EA was estimated for La^- and Ce^- based on their similar yields [3]. In 1998 the EA of lanthanum was measured using laser photoelectron spectroscopy and determined to be 0.47(2) eV [19]. Note that aside from the corelike Ce $4f^1$ subshell La and Ce have the same $5d^1 6s^2$ valence electron configuration and should behave very similar with regard to a *5d* attachment. Considering these independent experimental observations the EA of Ce (0.955 ± 0.026 eV) obtained by Davis and Thompson [1] seems to be quite high. On the other hand the present value (0.63 eV) is in reasonable agreement with the theoretical result (0.428 eV [2]) obtained by O'Malley and Beck. The

TABLE III. Electron affinities (eV) and *LS* composition for Ce^- bound states with *6p* attachment.

<i>J</i> level (<i>LS</i> %)	EA (this work)	EA [2]
$9/2(^2G85.27, ^2H13.03, ^4F1.39, ^4G0.27)$	0.156	0.349
$5/2(^4G63.60, ^2F36.38)$	0.080	
$7/2(^2H51.59, ^2G30.83, ^4G8.42, ^2F6.69, ^4F2)$	0.008	

discrepancy is partially due to the more accurate electron correlation treatment in the present calculations, cf. below.

For bound states formed by *6p* attachment, the ground state ($J=9/2$) was obtained in agreement with the result of O'Malley and Beck [2]. However, the EA (0.277 eV at the ACPF level) for the lowest bound state with *6p* attachment is about 0.072 eV lower than the result of O'Malley and Beck (0.349 eV). The discrepancy is due to the high complexity for $4f^1 5d^1 6s^2 6p^1$, i.e., O'Malley and Beck had convergence problems for Ce^- when using $4f^1 5d^1 6s^2 6p^1$ only, whereas we could not get a correct state average for the quartet state of $4f^1 5d^1 6s^2 6p^1$ at the CASSCF level without restricting the electron occupation number for the *4f*, *5d*, and *6p* shells.

Besides the approximations underlying our CASSCF MRCI treatment of correlation effects it is worthwhile to discuss the other possible sources of errors in our calculations. One can ask about the accuracy of the valence-only model Hamiltonian used in the pseudopotential calculations. It was previously found that the mean absolute errors for IP_1 (the first ionization potential) of lanthanides were 0.04 eV comparing the finite-difference pseudopotential complete open shell CI results with the all-electron MCDHF values based on the Dirac-Coulomb-Breit Hamiltonian [20]. For the EA of Ce we calculate -0.016 eV (-0.018 eV) at the all-electron MCDHF level using the Dirac-Coulomb (Dirac-Coulomb-Breit) Hamiltonian. Our corresponding finite difference pseudopotential complete open shell CI result of -0.004 eV agrees within two hundredths of an electron volt with the all-electron values proving the reliability of the applied pseudopotential. A second check has to be performed on the applied valence basis sets. The studies of ionization potentials of lanthanides showed that no corrections for basis set effects have to be applied if an accuracy of 0.1 eV is aimed for [20]. In case of EA of Ce our spin-orbit corrected CASSCF result of 0.067 eV also deviates less than 0.1 eV from the all-electron values.

Finally we checked the effect of ignoring excitations from the *4d* shell. For $Ce^- f^1 d^2 s^2 {}^2G$ and $Ce f^1 d^1 s^2 {}^1G$ besides the closed *4s*, *4p*, *4d*, *5s*, *5p* orbitals we also let the *6s* orbital doubly occupied and performed MRCI (ACPF) calculations in the $(14s13p10d8f6g)/[6s6p5d4f3g]$ standard basis sets

with two different core choices, i.e., $4d$ in/out of the core. The EA is increased (decreased) by 0.05 (0.01) eV with $4d$ in the core. We note here in passing that attributing the $5s$, $5p$ orbitals to the core leads to a decrease of 0.21 (0.27 eV) in corresponding calculations. Therefore our final estimate for the EA of Ce is 0.58 ± 0.10 eV. Since the errors in the valence-only Hamiltonian and the finite basis sets make a slight overestimation of the EA by up to 0.1 eV more likely than an underestimation, our result is consistent with the all-

electron value 0.428 eV obtained by O'Malley and Beck [2]. Note that these authors include at most g orbitals in their virtual space, a restriction for which we find a 0.07 eV lower EA compared to our current extrapolated value.

Taking all possible errors into account, we predict that Ce^- has at least 11 and 2 bound states arising from d and p attachment, respectively. Future experimental and theoretical work has to show if the two most weakly bound states found here are stable in reality.

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- [1] V. T. Davis and J. S. Thompson, Phys. Rev. Lett. **88**, 073003 (2002).
- [2] S. M. O'Malley and D. R. Beck, Phys. Rev. A **61**, 034501 (2000).
- [3] M.-J. Nadeau, M. A. Garwan, X.-L. Zhao, and A. E. Litherland, Nucl. Instrum. Methods Phys. Res. B **123**, 521 (1997).
- [4] D. Berkovits, S. Ghelberg, O. Herber, and M. Paul, Nucl. Instrum. Methods Phys. Res. B **123**, 515 (1997).
- [5] R. J. Zollweg, J. Chem. Phys. **50**, 4251 (1969).
- [6] B. M. Angelov, Chem. Phys. Lett. **43**, 368 (1976).
- [7] S. Bratsch, Chem. Phys. Lett. **98**, 113 (1983).
- [8] K. Dinov, D. R. Beck, and D. Datta, Phys. Rev. A **50**, 1144 (1994).
- [9] X. Cao and M. Dolg, J. Chem. Phys. **115**, 7348 (2001).
- [10] X. Cao and M. Dolg, Chem. Phys. Lett. **349**, 489 (2001).
- [11] M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **90**, 1730 (1989).
- [12] P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **115**, 5053 (1985).
- [13] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988).
- [14] P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988).
- [15] P. J. Knowles and H.-J. Werner, Theor. Chim. Acta **84**, 95 (1992).
- [16] B. O. Roos and P. R. Taylor, Chem. Phys. **48**, 157 (1980).
- [17] R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Lett. **143**, 413 (1988).
- [18] P. E. M. Siegbahn, Chem. Phys. Lett. **55**, 386 (1978).
- [19] A. M. Covington, D. Calabrese, J. S. Thompson, and T. J. Kvale, J. Phys. B **31**, L855 (1998).
- [20] X. Cao and M. Dolg, Mol. Phys. **101**, 961 (2003).
- [21] K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, and E. P. Plummer, Comput. Phys. Commun. **55**, 425 (1989).