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Relativistic coupled-cluster method: Intrashell excitations in the f^2 shells of Pr^{+3} and U^{+4}

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The relativistic Fock-space coupled-cluster method for the direct calculation of ionization potentials and excitation energies (including fine structure) is applied to the $4f^2$ levels of Pr^{+3} and the $5f^2$ levels of U^{+4}. The no-pair Dirac-Coulomb-Breit Hamiltonian is taken as the starting point. Correlation is treated by the coupled-cluster singles-and-doubles approximation, which includes single and double virtual excitations in a self-consistent manner, incorporating therefore the effects of the Coulomb and Breit interactions to all orders in these excitations. Extensive basis sets of kinetically balanced four-component Gaussian spinors are used to span the atomic orbitals. All levels appear in correct order. The average error of the excitation energies with the best basis is 222 cm^{-1} for Pr^{+3} and 114 cm^{-1} for U^{+4}. Fine-structure splittings are obtained with even better accuracy.

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I. INTRODUCTION

Experimental excitation energies of atoms and positive ions are known for many systems. This information is less readily available for lanthanides [1], and even more scarce for actinides [2–5]. The excitation energies of most multiply charged ions of these elements have been derived from absorption and fluorescence spectra of crystals containing the ions as impurities. The f^n spectra obtained this way may differ from those of the free ions because of the crystal field effects, which change the relative positions of the terms and split energy levels into their Stark components. Measuring the free-ion spectra of these elements is technically difficult. It is, therefore, desirable to develop a reliable high-precision *ab initio* method for the theoretical investigations of these systems.

Atomic systems with open-shell f^n configurations are highly relativistic and many electron in character. Relativistic and correlation effects are strongly intertwined, and the spectra of the f^n systems are, therefore, rather complicated. In particular, the fine-structure splittings are often comparable to differences between LS terms; not infrequently, fine-structure manifolds belonging to different LS terms overlap. In the nonrelativistic approach, fine-structure effects are attributed to "spin-orbit" interactions. While in many light elements these effects may be qualitatively modeled by perturbation theory or pseudopotential techniques, only computational methods including on equal footing both relativistic and correlation effects from the outset may be expected to provide quantitatively accurate atomic spectra for the systems under consideration.

The past few years have seen an intensive development of relativistic many-body techniques in quantum chemistry, in particular the method of fully relativistic (Dirac-equation based) coupled-cluster (RCC) theory [6–15]. The coupled cluster is an all-order method, and yields upon iteration the order-by-order many-body perturbation theory (MBPT). Infinite subclasses of perturbation diagrams are summed, and size extensivity is maintained. The latter feature is particularly important for heavy elements, which are also elements where relativistic effects are most significant. An additional advantage of the CC approach is connected with the similarity of CC and MBPT expansion terms. Using this property one can, if necessary, improve the CC results by adding the most important omitted diagrams with the aid of low-order MBPT. The RCC method gives both electron correlation and relativistic effects with high accuracy, and is a powerful and systematic method for calculating properties of heavy atomic and molecular systems.

The implementation of relativistic CC may be done either numerically [7] or by using discrete basis sets, which may be local [8,9] or global [10–15]. We have recently developed and implemented a relativistic version of the multireference valence-universal Fock-space coupled-cluster method, using a discrete basis of four-component Gaussian spinors (G spinors), which may also be applied to molecular systems. The method is based on the Dirac-Coulomb-Breit (DCB) Hamiltonian, and incorporates the instantaneous Coulomb and low-frequency Breit interactions to all orders. Accurate ionization potentials, excitation energies and fine-structure splittings were obtained for Au [12], highly ionized atoms with two to five electrons [13], and the alkali-metal atoms Li to Fr [14]. More recently, pair correlation energies (both relativistic and nonrelativistic) were calculated for all the

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electron pairs of the Xe atom [15].

The previous applications were limited to systems with s, p, and d valence electrons. Here the method is employed to f^2 shells, namely, the $4f^2$ configuration of Pr^{+3} and $5f^2$ of U^{+4}. These configurations yield complex structures and present a challenge to theory. An additional motivation for studying these systems is that their spectra are well characterized experimentally [1,5], while extensive computational treatments are scarce. Several *ab initio* calculations exist for Pr^{+3}. Early work includes nonrelativistic second-order MBPT [16] and nonrelativistic configuration interaction (CI) [17]. More recently, Cai *et al.* [18] carried out a large-scale multiconfigurational Dirac-Fock (MCDF) study with several thousand configuration state functions, using the modified GRASP [19] computer code. We are not aware of *ab initio* calculations on the U^{+4} system.

II. METHOD

The relativistic coupled-cluster method has been described in our previous publications [12,14], and only a brief review is given here. We start from the projected Dirac-Coulomb (or Dirac-Coulomb-Breit) Hamiltonian advocated by Sucher [20],

$$H_+ = H_0 + V, \tag{1}$$

where (in atomic units)

$$H_0 = \sum_i \Lambda_i^+ h_D(i) \Lambda_i^+, \tag{2}$$

$$h_D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_{\text{nuc}}(i) + U(i), \tag{3}$$

$$V = \sum_{i<j} \Lambda_i^+ \Lambda_j^+ (V_{\text{eff}})_{ij} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+. \tag{4}$$

Here h_D is the one-electron Dirac Hamiltonian. An arbitrary potential U is included in the unperturbed Hamiltonian H_0 and subtracted from the perturbation V. This potential is chosen to approximate the effect of the electron-electron interaction; in particular, it may be the Dirac-Fock self-consistent-field potential. The nuclear potential V_{nuc} includes the effect of finite nuclear size. The Λ_i^+ are projection operators onto the positive energy states of the Dirac Hamiltonian h_D. Because of their presence, the Hamiltonian H_+ has normalizable, bound-state solutions. This approximation is known as the no-(virtual)-pair approximation, since virtual electron-positron pairs are not allowed in intermediate states. The form of the effective potential V_{eff} depends on the gauge used. In Coulomb gauge it becomes (in atomic units, correct to second order in the fine-structure constant α) [6]

$$V_{\text{eff}} = \frac{1}{r_{12}} + B_{12} + O(\alpha^3), \tag{5}$$

where the frequency-independent Breit interaction is

$$B_{12} = -\frac{1}{2r_{12}} [\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})/r_{12}^2]. \tag{6}$$

In q-number theory the Dirac-Coulomb-Breit Hamiltonian H_+ is rewritten in terms of normal-ordered products of the spinor operators, $\{r^+s\}$ and $\{r^+s^+ut\}$ [20,21],

$$\begin{aligned} H &= H_+ - \langle 0|H_+|0\rangle \\ &= \sum_{rs} f_{rs}\{r^+s\} + \frac{1}{4}\sum_{rstu} \langle rs||tu\rangle \{r^+s^+ut\}, \end{aligned} \tag{7}$$

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 operators Λ^+ is now taken over by the 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 [22], the effective Hamiltonian has the form

$$H_{\text{eff}} = PH\Omega P, \tag{8}$$

where Ω is the normal-ordered wave operator,

$$\Omega = \{\exp(S)\}. \tag{9}$$

The excitation operator S is defined in the Fock-space coupled-cluster approach 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,

$$S = \sum_{m\geq 0}\sum_{n\geq 0}\left(\sum_{l\geq m+n} S_l^{(m,n)}\right). \tag{10}$$

The upper indices in the excitation amplitudes reflect the partitioning of the Fock space into sectors, which correspond to the different numbers of electrons in the physical system. This partitioning allows for partial decoupling of the open-shell CC equations. The equations for the (m,n) sector involve only S elements from sectors (k,l) with $k \leq m$ and $l \leq n$, so that the very large system of coupled nonlinear equations is separated into

TABLE I. Basis sets for Pr and U. Members of the well-tempered s-basis series used in the various l sectors are given.

		Basis	Reference	s	p	d	f	g	h	i
Pr	1	$31s25p20d15f11g$	[25](basis 1)	1–31	5–29	8–27	13–27	16–26		
	2	$29s23p18d14f10g5h$	[25](basis 2)	1–29	5–27	8–25	13–26	16–25	19–23	
	3	$29s23p19d14f10g6h4i$	[25](basis 2)	1–29	5–27	8–26	13–26	16–25	19–24	21–24
U		$33s29p18d15f10g6h$	[26]	1–33	4–32	13–30	16–30	21–30	24–29	

smaller subsystems, which are solved consecutively: first, the equations for $S^{(0,0)}$ (corresponding to the reference determinant) are iterated to convergence; the $S^{(1,0)}$ (or $S^{(0,1)}$) equations are then solved using the known $S^{(0,0)}$, and so on. This separation, which does not involve any approximation, reduces the computational effort significantly. The eigenvalues of the effective Hamiltonian (8) in a sector give directly the correlated energies in that sector with respect to the correlated (0,0) reference state. These transition energies may be ionization potentials, electron affinities, or excitation energies, according to the presence of valence holes and/or valence particles.

In the present application, we use the (0,0), (0,1), and (0,2) sectors. The lower index l in (10) is truncated at l=2. The resulting CCSD (coupled cluster with single and double excitations) 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. Negative energy states are excluded from the Q space, and the diagrammatic summations in the CC equations are carried out only within the subspace of the positive energy branch of the DF spectrum.

III. CALCULATIONS

The Fock-space relativistic coupled-cluster method was applied to the f^2 configurations of Pr^{+3} and U^{+4}. The Dirac-Fock-Coulomb or Dirac-Fock-Breit equations were solved for the closed-shell systems Pr^{+5} and U^{+6}, which define the (0,0) sector. These systems were correlated by CCSD, and two electrons were then added, one at a time, to reach the f^2 configuration in the (0,2) sector.

The Dirac-Fock [21] and RCC [12,14] programs are both written for spherical symmetry, utilizing the angular decomposition of the wave function and CC equations in a central field. The energy integrals and CC amplitudes which appear in the Goldstone-type diagrams defining the CC equations are decomposed in terms of vector-coupling coefficients, expressed by angular-momentum diagrams, and reduced Coulomb-Breit or S matrix elements, respectively. The reduced equations for single and double excitation amplitudes are derived using the Jucys-Levinson-Vanagas theorem [22] and solved iteratively. This technique makes possible the use of larger basis sets.

To avoid "variational collapse" [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 [21]. The atomic masses used are 140.90 for Pr and 238.03 for U. The speed of light c is 137.037 atomic units. Nonrelativistic results were obtained with $c = 10^5$ a.u.

The uncontracted well-tempered basis sets of Huzinaga and Klobukowski [25] were used for Pr, and the universal basis set of Malli *et al.* [26] was selected for U. The basis

TABLE II. Ionization potential (IP) and excitation energies (EE) of Pr^{+3} $4f^2$ levels (cm^{-1}). MCDF — multiconfiguration Dirac-Fock [18]. DC I — relativistic coupled cluster with basis set I, starting from the Dirac-Coulomb Hamiltonian. DCB I — similar, starting from the Dirac-Coulomb-Breit Hamiltonian. The experimental results are from Ref. [1].

Level	Expt.	MCDF	DC 1	DC 2	DCB 2	DC 3
$^3H_4$ (IP)	314400	—	308636	310925	311794	311426
$^3H_5$	2152.09	2337	2273	2273	2081	2270
$^3H_6$	4389.09	4733	4645	4641	4250	4635
$^3F_2$	4996.61	4984	4749	4832	4842	4843
$^3F_3$	6415.24	6517	6266	6345	6215	6354
$^3F_4$	6854.75	6950	6808	6844	6680	6843
$^1G_4$	9921.24	10207	10019	10014	9686	10001
$^1D_2$	17334.39	18153	16803	16961	16867	16998
$^3P_0$	21389.81	22776	20802	21109	21128	21155
$^3P_1$	22007.46	23450	21443	21747	21713	21791
$^1I_6$	22211.54	25854	22267	22061	21829	22010
$^3P_2$	23160.61	24653	22719	23009	22803	23051
$^1S_0$	50090.29	50517	48448	49072	49061	49194
Average error (EE's)		853	394	245	313	222

TABLE III. Fine structure in Pr^{+3} (cm^{-1}). The experimental results are from Ref. [1].

	Expt.	MCDF	DC 1	DC 2	DCB 2	DC 3
${}^3H_5 - {}^3H_4$	2152	2337	2273	2273	2081	2270
${}^3H_6 - {}^3H_5$	2237	2396	2369	2368	2169	2365
${}^3F_3 - {}^3F_2$	1419	1533	1517	1513	1373	1511
${}^3F_4 - {}^3F_3$	440	433	542	499	465	489
${}^3P_1 - {}^3P_0$	618	674	631	638	585	636
${}^3P_2 - {}^3P_1$	1153	1203	1276	1262	1090	1260
Average error		95	98	89	51	86

sets are summarized in Table I. They go up to i orbitals ($l = 6$) for Pr and h orbitals ($l = 5$) for U. 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 correlated shells are $4spdf5sp$ for Pr and $4f5spdf6sp$ for U. The virtual orbitals with high orbital energies have been found to contribute very little to correlation effects on excitation energies; orbitals higher than 100 a.u. are therefore eliminated from the calculation, effecting considerable savings in computational effort. All computations were carried out on the IBM RS6000/360 computer workstation at Tel Aviv University.

IV. RESULTS AND DISCUSSION

A. Pr^{+3}

The ionization potential and excitation energies of Pr^{+3} are shown in Table II. The Dirac-Coulomb results are given in the three bases of Table I, which go up to $l = 4$, 5, and 6. The addition of i functions changes the excitation energies by 50 cm^{-1} or less, indicating convergence with respect to l. The ionization potential, on the other hand, changes by 500 cm^{-1}, and higher l values may be needed for better convergence. The IP also shows a larger effect of the Breit term than the excitation energies.

The calculated transition energies are compared with experiment [1] and with the extensive numerical MCDF calculations of Cai *et al.* [18]. The excitation energies are in very good agreement with experiment. All f^2 levels appear in the correct order; the average error for the largest basis is 222 cm^{-1}. A full third of the total error comes from the very high ${}^1S_0$ state, which is off by 900 cm^{-1}; the next highest error is 335 cm^{-1}, for the ${}^1D_2$ level. The RCC results are better than numerical MCDF [18], which gives errors four times higher than ours (up to 3600 cm^{-1} for ${}^1I_6$, average error 853 cm^{-1}) and incorrect ordering of the ${}^1I_6$ and ${}^3P_2$ levels. Apparently, the MCDF function does not include sufficient dynamical correlation, which has a significant effect on the excitation energies. The effect of the Breit term on the excitation energies is not very large. The computed ionization potential is less accurate. As noted above, the IP shows slower convergence with respect to the basis and a larger effect of the Breit interaction.

The fine-structure splittings are very close to experiment (see Table III). Convergence with respect to basis (or to the l expansion) is even better than for the excitation energies. The relatively large effect of the Breit interaction, which improves the results significantly, should be noted. A similar phenomenon has been observed for other systems [12,14]. The distortion of MCDF fine-structure splittings by "spurious correlation," observed by Huang *et al.* [27], does not occur in the RCC method. This distortion leads to artificial splittings in the nonrelativistic limit, when c goes to infinity. Exact degeneracy is obtained in our calculations at this limit.

Comparison with nonrelativistic results can be made only for the LS term averages (Table IV). The errors in the nonrelativistic CI [17] and perturbation [16] calculations are largely due to the size of the basis used. Comparison of relativistic and nonrelativistic CC computations with the same basis reveals a very large change (>3 eV) in the ionization potential, with a much smaller effect on the term energy differences. The insufficient inclusion of dynamical correlation in the MCDF function leads again to significant errors.

B. U^{+4}

The basis used (Table I) included functions with l up to 5, which proved adequate for Pr^{+3}. The ionization potential and excitation energies in the $5f^2$ configuration

TABLE IV. LS term averages in Pr^{+3}: Relativistic vs nonrelativistic (cm^{-1}). The experimental results are from Ref. [1]. The configuration-interaction (CI) results are from Ref. [17], and the second-order perturbation theory results (PT-2) are from Ref. [16].

Term	Expt.	Relativistic			Nonrelativistic		
		MCDF	DC 2	DCB 2	NRCC 2	CI	PT-2
${}^3H$ (IP)	316846		313511	314162	341725		
${}^3F$	3819	3696	3613	3719	4373	5022	5115
${}^1G$	7457	7566	7428	7300	6454	5540	6623
${}^1D$	14888	15511	14375	14481	15563	17745	18419
${}^1I$	19765	23212	19745	19461	20686	23130	26725
${}^3P$	20133	21402	19677	19868	20867	23927	25789
${}^1S$	47644	47875	46486	46693	49719	48644	54794
Average error (EE's)		965	442	364	994	2356	4238

are shown and compared with experiment [5] in Table V. Agreement with experiment is again very good, with an average error of 206 cm^{-1} without and 114 cm^{-1} with the Breit interaction, and a maximum error of 330 cm^{-1}. All levels appear in correct order. The agreement is better than for Pr^{+3}, partly because no experimental value is known for the $^1S_0$ level, which contributes heavily to the average error in the lighter atom. Possible sources of the remaining errors are high-order QED effects, deficiencies in the basis, and the truncation of the coupled-cluster expansion.

V. SUMMARY AND CONCLUSION

The relativistic open-shell coupled-cluster method was applied to the direct calculation of ionization potentials and excitation energies in the f^2 configuration of Pr^{+3} and U^{+4}. Sizable basis sets of four-component Gaussian spinors were used, with highly satisfactory excitation energies and fine-structure splittings in both atoms. The ionization potential of Pr^{+3} is less accurate and requires further investigation. Inclusion of the Breit interaction to all orders leads to significant improvement in the fine-structure splittings of the two atoms and in the excitation energies of U^{+4}.

TABLE V. Excitation energies of U^{+4} $5f^2$ levels (cm^{-1}). The experimental results are from Ref. [5].

Level	Expt.	DC	DCB
$^3H_4$ (IP)		380485	381336
$^3F_2$	4160.65	4084	4090
$^3H_5$	6136.88	6233	6029
$^3F_3$	8983.53	9025	8848
$^3F_4$	9433.76	9585	9399
$^3H_6$	11513.58	11711	11354
$^1D_2$	16465.30	16554	16407
$^1G_4$	16655.73	16929	16544
$^3P_0$	17128.16	17471	17460
$^3P_1$	19818.58	20145	20016
$^1I_6$	22276.05	22581	22319
$^2P_2$	24652.91	24979	24648
$^1S_0$		46230	46059
Average error		206	114

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