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REGULAR ARTICLE

Effect of electron correlation on the Pa atom energy levels and electron coupling

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Abstract The lower energy levels of the protactinium (Pa) atom are unusually difficult to treat theoretically. Pa is located where the 6*d* and 5*f* energies cross; simple calculations consistently put the electron configurations $5f^16d^27s^2$ and $5f^26d^17s^2$ in the incorrect order. We have used multireference spin–orbit configuration interaction to compute the energies of these states to determine which additional interactions need to be included. We also discuss the less common J_1j coupling scheme suggested for these atomic states with applications also to the $5f^16d^2$ and $5f^26d^1$ states of Pa^{2+}.

Keywords Electron coupling · Electron correlation energy · Energy levels of atoms · Atomic spectra

1 Introduction

The compendium of atomic energy-level data by the National Institute of Science and Technology (NIST) [1] points out that the Pb, Bi, and Po atoms are best described by *jj* coupling and that the Pa, U, and Np atoms are best described by J_1j coupling [2–4], a less well-known coupling scheme. The protactinium atom (Pa), in particular, has an additional complication in that it is located in the periodic table where the 5*f* and 6*d* shells are almost degenerate in energy. The electron configurations involved for Pa are $5f^26d^17s^2$ and $5f^16d^27s^2$. Experimental results established that the ground state ($J = 11/2$) is from the first electron configuration and that the lowest state of the second electron configuration ($J = 7/2$) is 1,978 cm^{-1} higher in energy [5, 6].

An early relativistic calculation [7] on Pa gave the lowest $5f^16d^27s^2$ state as the ground state by 7,000 cm^{-1}. Although details of this calculation are not available, relativistic electronic structure software at this time (1969) usually included little or no electron correlation energy. This energy difference is small on an electronic energy scale; thus, it is not too surprising that this level of calculation, which usually gives correct results, does not do so here. Another example of this difficulty is the ground state of Rf [8].

A later Pa calculation included electron correlation for the 6*s*, 6*p*, 5*d*, and 5*f* shells using the computationally efficient averaged coupled-pair functional (ACPF) [9] method and treating the spin–orbit interaction in a separate calculation. The lowest $5f^26d^17s^2$ state was obtained as the ground state, 2,800 cm^{-1} below the lowest $5f^16d^27s^2$ state [10].

The Pa^{2+} ion has similar electronic states, but without the $7s^2$ shell. The ground state has the $5f^26d^1$ electron configuration [11] and $J = 11/2$, but the excitation energy to the lowest state from the $5f^16d^2$ electron configuration has not been measured. Estimates [12] based on an early non-relativistic calculation [13] gave the lowest $5f^3$ state at 4,500 ± 1,000 cm^{-1} and the lowest $5f^16d^2$ state at 10,000 ± 6,000 cm^{-1}, but use of the Schrödinger equation for actinides has been shown to be inadequate [14, 15]. A particular example is the inaccurate non-relativistic relative energy of the 5*f* and 7*s* shells in actinides. Non-relativistic energy expressions continue to be useful in semi-empirical

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Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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calculations [11], but the values of the parameters cannot be obtained from non-relativistic theory.

2 J_1j Coupling

The J_1j coupling scheme requires at least two open shells. The notation implies that the second open shell contains only one electron as is the case for Pa and most other cases that have been discussed, but in a more general case, such as $4f^{13}6s^16p^1$, the more general notation J_1J_2 is used [3]. The interaction inequalities are

$$\begin{aligned}&\text{intrashell electron repulsion splittings} >\\ &\quad\text{spin-orbit splittings} >\\ &\text{intershell electron repulsion splittings}\end{aligned}$$

Thus, *LS* coupling is used to form *L*, *S*, *J* quantum numbers for each shell, and then the two *J* values are coupled to give a total *J*, and there are, in general, no good overall *L*, *S* quantum numbers. Notation can be of the form $[(nl)^x(S_1, L_1, J_1)(n'l'j)]_J$

A simple test is to use this coupling scheme to calculate g values. Judd [2] showed that for Pa, U, and Np (electron configurations $5f^x6d^17s^2$) J_1j coupling produces more accurate g values than does *LS* coupling. Another comparison is whether J_1j coupling groups the energy levels into narrower energy ranges than other coupling schemes. This criterion has been applied to the U atom, where the result has been described as reasonably good but not perfect. J_1j coupling has mostly been applied to ground electron configurations of actinides and to Rydberg excited electron configurations of lanthanides [3, 4].

For the lower energy Pa cases, we have

$$\left[5f^2(^3H_4)6d_{3/2}\right]_{\{11/2\},9/2,7/2,5/2}$$

$$\left[6d^2(^3F_2)5f_{5/2}\right]_{9/2,\{7/2\},5/2,3/2,1/2}$$

where the *J* value for the lowest state is indicated by braces.

3 Methods

We applied multireference spin–orbit single- and double-excitation configuration interaction (SOCISD) to the calculation of the lowest Pa (and Pa^{2+}) states. Relativistic effects were included by means of relativistic effective core potentials (RECPs), including accompanying effective spin–orbit operators [16, 17]. Contracted Gaussian basis sets were used. The Columbus suite of computer programs [18] was used for these calculations.

We used an RECP with a 68-electron core (RECP68) with 23 explicitly treated electrons, developed by Christiansen [19], and an RECP with a 60-electron core (RECP60) with 31 explicitly treated electrons, developed by the Stuttgart–Dresden–Bonn group [20]. The goals in the choice of core size [16] are to include all low-energy, small-radius electron shells in the core and treat all high-energy, larger-radius electron shells explicitly. The complication in heavier elements is medium-energy, larger-radius shells, which can be influenced to some extent by bonded atoms and by the highest-energy, similar-radius (valence) shells; such shells are often referred to as outer core shells and some or all of them need to be treated explicitly. For Pa, both RECPs have the $1s\ldots4f$ shells in the core and the $5d$, $6s$, $6p$, $5f$, $6d$, $7s$ shells are treated explicitly. The 68-electron core includes the $5s$ and $5p$ shells (much lower energy than $5f$), while the 60-electron core treats these shells explicitly (similar radius means large exchange integrals). We use both RECPs in order to see the effect of core size on the energy differences of primary interest. RECPs are often compared with respect to bond distances and other properties as well.

Contracted basis sets of sizes cc-pVDZ and cc-pVTZ (correlation-consistent polarized valence double-, triple-zeta) were developed [21] for both RECPs using the ATMSCF program [22]. This program uses *LS* coupling, but was the most readily applied. The primitive Gaussians were optimized for the $5f^26d^17s^17p^1$ lowest LS state so that a basis set for the $7p$ shell was included. The zeta values for the *g* and *h* functions were optimized in SOCISD calculations on the ground state of the Pa atom. The basis set sizes are

RECP68-DZ: (6s6p6d4f1g)/[4s4p4d2f1g]
RECP60-DZ: (8s8p6d4f1g)/[6s6p4d2f1g]
RECP68-TZ: (9s9p9d6f2g1h)/[6s6p6d3f2g1h]
RECP60-TZ: (12s12p12d6f2g1h)/[9s9p6d3f2g1h]

The orbitals for use in the configuration interaction calculations were obtained by optimizing the average quartet energies of the respective electron configurations [23], since the lower energy states of each configuration were expected to contain more quartet than doublet character. This process permits all the orbitals to adjust their radial distribution for each electron configuration and should materially reduce any bias introduced by choosing the orbital exponents to minimize the energy of a particular state.

The reference configurations for the configuration interaction (CI) calculations were spin-eigenfunctions (configuration state functions, CSFs) for the $5f^26d^1$ and $5f^16d^2$ open shells. There are 455 and 315 of these, respectively. The initial calculations for Pa were to correlate the five valence shell electrons ($5f$, $6d$, $7s$) only. All single- and double-excitation CSFs were used, so that no assumptions about electron coupling schemes were made. It should be noted that the electron configurations have opposite parity so their wave functions do not mix. The number of CSFs was 5.5 million in the largest case, but always more for $5f^26d^17s^2$ than for $5f^16d^27s^2$ because the number is roughly proportional to the number of references.

Next, we added intershell electron correlation between the outer core shells and the valence shells. This was done by adding double-excitation CSFs with one excitation out of a valence shell and the other excitation out of an outer core shell. The additional CSFs for Pa involved numbers in the 200 million range, which we could not handle conveniently all at once, so we considered one outer core shell at a time. A few preliminary combined calculations showed that summing the individual outer-core shell correlation energies overestimated the total correlation energies by 3-5% but gave values for the importance of the individual shells.

4 Pa results and discussion

For both RECPs and both basis sets, the valence-shell CI calculations give the excitation energy

$$\Delta E = (\text{lowest } 5f^16d^27s^2 \text{ energy}) - (\text{lowest } 5f^26d^17s^2 \text{ energy})$$

as negative (Table 1), as did the earlier calculation [7], in major disagreement with the experimental value. Adding intershell correlation turns ΔE positive but larger than the experimental value.

All the final ΔE values included correlation energy with all the outer core shells and are several thousand cm^{-1} larger than the experimental value of 1,978 cm^{-1}, with the TZ values larger than the DZ values (general increase in all correlation energies) and the RECP60 values larger than the RECP68 values (due to inclusion of $5p$ contributions).

Table 1 ΔE, Pa excitation energy (cm^{-1}), including successive outer-shell correlation energy with valence shells

Shells	RECP-basis set			
	60-DZ	60-TZ	68-DZ	68-TZ
Valence	−1,639	−2,332	−2,763	−2,879
+$5s$	−1,613	−2,264	–	–
+$5p$	20	−57	–	–
+$5d$	3,715	5,731	1,314	3,589
+$6s$	4,224	6,452	1,824	4,237
+$6p$	6,140	8,278	3,810	6,206

Table 2 Pa intershell correlation energy contributions (hartree), for RECP60, DZ and TZ

Shell	DZ	TZ
$5s$	−0.000495	−0.001045
$5p$	−0.196348	−0.287144
$5d$	−0.077076	−0.105879
$6s$	−0.011571	−0.016784
$6p$	−0.208619	−0.261233

Table 2 shows the intershell correlation energies by outer core shell for the $5f^26d^17s^2$ ground state for RECP60. They increase with basis set size as expected. The largest correlation energies are with the $5p$ and $6p$ shells, followed by the $5d$, $6s$, and $5s$ shells, but the largest contribution to the excitation energy, as shown in the differences in Table 1, is from the correlation energy with the $5d$ shell, with the $6p$ and $5p$ contributions next in size. The $6s$ shell contributes a smaller amount and the $5s$ shell has little effect. In general, correlation energies increase with basis set size and are slowly convergent [24].

The major effect that has still been omitted is the intrashell outer-core correlation energy. This is a large part of the total correlation energy, but is presumably somewhat less sensitive to changes in the occupation of the valence shells. For RECP60, all 31 electrons would need to be fully correlated, and for RECP68, all 23 electrons would need to be fully correlated. Such calculations would involve expansion lengths of a number of billions of CSFs, which we are unable to handle at present.

The earlier ACPF calculation [10] did not include electron correlation with the $5p$ shell, which has been shown here to be substantial. Thus, their value for the excitation energy would probably have been moderately higher if they had correlated this shell also, giving better agreement with our results.

5 Pa^{2+} results and discussion

The corresponding calculations for Pa^{2+} involve two fewer valence electrons and were done in the same manner. The computed excitation energies are shown in Table 3. An earlier calculation on the ground state of Pa^{2+} was carried out [16] in studying ionization potentials, but did not include excited states. LS coupling was used to describe the wave function and the particular difficulty in computing energy differences between states with different occupation numbers of f shells was described.

Table 3 ΔE, Pa^{2+} excitation energy (cm^{-1}), including successive outer-shell correlation energy with valence shells

Shells	RECP-basis set			
	60-DZ	60-TZ	68-DZ	68-TZ
valence	8,102	5,935	6,178	5,389
$+5s$	8,141	6,033	–	–
$+5p$	9,451	7,580	–	–
$+5d$	13,731	13,956	10,723	12,532
$+6s$	14,511	15,004	11,488	13,523
$+6p$	15,431	15,366	12,327	14,329

The absence of the $7s^2$ shell results in the $5f^26d^1$ lowest state being lower than the $5f^16d^2$ lowest state even when including valence-shell correlation only. The final calculated excitation energies increase to the 12,000 to 15,000 cm^{-1} range as the correlation between outer core shells and valence shells is included. There is no experimental value yet for this excitation energy for comparison; thus, as with the corresponding Pa values, we expect our computed ΔE values to be several thousand cm^{-1} too high. With two fewer electrons, we could include, for the RECP60-DZ calculations, all the outer core shells at once, obtaining a ΔE value of 13,274 cm^{-1} and reductions in the outer-core correlation energy with the valence shell of 6-8% compared with calculating this quantity shell-by-shell. For the lowest $5f^26d^1$ state the J value was 11/2, the same as for Pa, while for the lowest $5f^16d^2$ state the J value was 9/2 at the valence correlation level, but became 7/2, the same as for Pa, as correlation with the outer core shells was added.

We computed a number of excited states of both parities for the RECP60-DZ wave functions; the energies are given in Table 4. The resulting sets of J values for each parity closely resemble the corresponding lists [11] for Pa. The J value of 13/2 for the highest even parity state is not well established because with our programs we could not easily obtain additional energies, which, if degenerate, would mean a higher J value, but this is unlikely.

A simple comparison for J_1j coupling is to use a crude model involving only the one-electron spin–orbit parameters ζ_{nl} to calculate [25] the spin–orbit energy for the lower states of each parity, assuming that $\zeta_{5f} = \zeta_{6d}$ (sample [26] ζ_{5f}, ζ_{6d} values for U are 1,734, 1,303 cm^{-1}), as shown in Table 5.

The difference between the first two approximate spin–orbit energies is larger for the even parity states (2.5ζ vs. 1.5ζ) and the (four) J values for the lowest even spin–orbit energy are the same as the first four J values that we compute for Pa^{2+} (Table 4) and are the same as measured [11] for Pa, supporting the J_1j coupling model for the lowest even set of states [2, 3]. For the odd parity states, the spin–orbit energy difference between the lowest sets of states is smaller and the description is more complicated. The first three J values correspond to the lowest spin–orbit set, but three levels from the second set are present before the last two levels from the first set appear. The odd states with J values of 1/2 or 3/2 are not present in the experimental list of low-energy odd states for Pa. A calculation of the odd parity states of Pa with valence correlation only gave the same low-J values in similar positions on the list; thus, it seems likely that these levels were missed by the experimental techniques used [27]. They may not be in the exact order given by our calculations, but it seems unlikely that they are in greatly different positions.

Table 4 Pa^{2+} excitation energy (cm^{-1}) with RECP60-DZ, including outer-shell correlation energy with valence shells

Even parity		Odd parity	
J	ΔE	J	ΔE
11/2	0	7/2	13,274
9/2	800	9/2	14,661
5/2	1,876	1/2	16,217
7/2	3,829	9/2	17,668
9/2	3,928	7/2	18,861
11/2	4,343	11/2	19,421
13/2	4,557	3/2	20,548
		5/2	20,690
		9/2	20,724

Table 5 Lowest approximate spin–orbit energies

electron configuration	spin–orbit energy	J values
even parity		
$[5f^2(^3H_4)6d_{3/2}]$	-4.5ζ	11/2, 9/2, 7/2, 5/2
$[5f^2(^3H_4)6d_{5/2}]$	-2ζ	13/2, 11/2, 9/2, 7/2, 5/2, 3/2
$[5f^2(^3H_5)6d_{3/2}]$	-2ζ	13/2, 11/2, 9/2, 7/2
odd parity		
$[6d^2(^3F_2)5f_{5/2}]$	-4ζ	9/2, 7/2, 5/2, 3/2, 1/2
$[6d^2(^3F_3)5f_{5/2}]$	-2.5ζ	11/2, 9/2, 7/2, 5/2, 3/2, 1/2

6 Conclusions

We have shown that for Pa and Pa^{2+} it is necessary that the correlation energy between outer core shells and valence shells be included in any calculation of their electronic states, but that including these interactions is not sufficient to obtain accurate values for the energy differences. The energy levels of Pa^{2+} are very similar to those of Pa, except that the odd parity states for $Pa^{2+}$are all at somewhat higher energy than those of Pa. We suggest that some odd parity states of Pa with low J values have not yet been found experimentally. The electron coupling for both Pa and $Pa^{2+}$is best described by J_1j coupling.

To obtain better accuracy, we would need to fully correlate 33 electrons for Pa and 31 electrons for Pa^{2+} with at least a TZ basis set. The additional correlation energy that would be included is the intrashell correlation energy of the outer core shells. Although this is a large part of the overall correlation energy, it is presumably the least sensitive part to excitations in the valence shells, but its changes are still large enough to be necessary for obtaining accurate excitation energies. We have used a single-processor version of the Columbus programs for these calculations; a highly parallel version of the Columbus programs exists [28, 29], but its spin–orbit CI feature is not yet ready. Calculations fully correlating similar numbers of electrons have been made by Fock-space, coupled-cluster methods with four-component spin orbitals [30], but these methods so far have only been programmed for open-shell cases with at most two electrons outside of closed shells or two electrons missing from closed shells, while the Pa and Pa^{2+} cases would need three electrons outside a closed shell. We look forward to seeing Pa and Pa^{2+} calculations being carried out with improved accuracy in the future.

A question that naturally arises is why there is more intershell correlation energy in the f^2d^1 states than in the f^1d^2 states. A pertinent aspect of these electronic configurations is the number of ways to arrange the electrons in them, 455 vs. 315, respectively, which are therefore the numbers of references. The number of correlating CSFs being approximately proportional to the number of references, the f^2d^1 states will tend to have more correlation energy with outer core shells even if the correlating CSFs vary somewhat in their effectiveness.

This work provides a comparison of the accuracy of using an RECP with a 60-electron core and one using a 68-electron core. The additional shells in the outer core for RECP60, 5*s* and 5*p*, contribute quite differently to the overall correlation energies and the excitation energies. The 5*s* contribution is quite small, while the 5*p* contribution is large and about the same size as that of the 6*p* shell. This result suggests that for studying actinide atomic excitation energies, RECPs with 60 or 62 electrons in the core should be used.

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References

1. Martin WC, Wiese WL Atomic spectroscopy: a compendium of basic ideas, notation, data, and formulas; Chapters 9, 11. http://www.nist.gov/physlab/pubs/atspec/index.cfm
2. Judd BR (1962) Phys Rev 125:613–625
3. Wybourne BG (1965) Spectroscopic properties of rare earths. Interscience, New York, pp 51–68
4. Wybourne BG, Smentek L (2007) Optical spectroscopy of lanthanides: magnetic and hyperfine interactions. CRC, Boca Raton, FL, pp 44–50
5. Giacchetti A, Blaise J (1970) Private communication to Brewer L (1971) J Opt Soc Am 56:1101–1111
6. Blaise J, Ginibre A, Wyart J-F (1985) Z Phys A Atoms Nuclei 321:61–63
7. Maly J (1969) cited by Cauchois Y Tagungsher Int. Pa-Konf. Born H-J Ed.; Schloss-Elmau, April 15–18. German Report BMBW-FBK 71-17
8. Eliav E, Kaldor U, Ishikawa Y (1995) Phys Rev Lett 74:1079–1082
9. Gdanitz RJ, Ahlrichs R (1988) Chem Phys Lett 143:413–420
10. Liu W, Küchle W, Dolg M (1998) Phys Rev A 58:1103–1110
11. Blaise J, Wyart J-F Selected constants, energy levels, and atomic spectra of actinides. http://www.lac.u-psud.fr/Database/Contents.html
12. Brewer L (1971) J Opt Soc Am 61:1666–1682
13. Wilson M (1967) J Opt Soc Am 57:429–430
14. Pitzer KS (1979) Acc Chem Res 12:271–276
15. Pyykkö P, Desclaux J-P (1979) Acc Chem Res 12:276–281
16. Dolg M, Cao X (2004) Recent Adv Comput Chem 5:1–35
17. Ermler WC, Ross RB, Christiansen PA (1988) Adv Quantum Chem 19:139–182
18. Lischka H, Shepard R, Pitzer RM, Shavitt I, Dallos M, Müller T, Szalay PG, Seth M, Kedziora GS, Yabushita S, Zhang Z (2001) Phys Chem Chem Phys 3:664–673
19. Christiansen PA (1999) Private communication to Pitzer, RM. Available at http://www.web.chemistry.ohio-state.edu/pitzer/docs/arep/pa68
20. Küchle W, Dolg M, Stoll H, Preuss H (1994) J Chem Phys 100:7535–7542
21. Basis sets available at http://www.web.chemistry.ohio-state.edu/pitzer/basis_sets.html
22. Pitzer RM (2005) Comput Phys Commun 170:239–264
23. Pitzer RM Theoretical chemistry group report 101 (unpublished). Available at http://www.web.chemistry.ohio-state.edu/pitzer/docs/rpt101.pdf
24. Dunning TH (1989) J Chem Phys 90:1007–1023
25. Condon EU, Shortley GH (1935) The theory of atomic spectra. Cambridge University Press, London
26. Petit A (1999) Eur Phys J D 6:157–170
27. Wyart J-F (2010) Private communication to Pitzer RM
28. de Jong WA, Bylaska E, Govind N, Janssen CJ, Kowalski K, Müller T, Nielsen IMB, van Dam HJJ, Veryazov V, Lindh R (2010) Phys Chem Chem Phys 12:6896–6920
29. Mueller T (2009) J Phys Chem A 113:12729–12740
30. Kaldor U (1997) In: Recent advances in coupled-cluster methods. Bartlett RJ Ed.; World Scientific, Singapore