## On the calculation of multiplet energies of three-open-shell $4f^{13}5f^{n}6d^{1}$ electron configuration by LFDFT: modeling the optical spectra of 4f core-electron excitation in actinide compounds

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**Electronic Supplementary Information ESI (6 pages)** 



**Fig. S1** LFDFT results of free U<sup>4+</sup> ion obtained from DFT calculation using the LDA SVWN functional, showing the multiplet energies of the configuration  $4f^{13}5f^26d^1$  (in red) and intensity of the  $5f^2 \rightarrow 4f^{13}5f^26d^1$  transitions, *i.e.* oscillator strengths (in black) and Lorentzian broadening (in grey) (a) and the deconvolution of the intensity as function of final electronic states with J = 3 (in magenta), J = 4 (in blue) and J = 5 (in green) values (b). In the ordinates, the intensity plots are given in arbitrary unit.



**Fig. S2** LFDFT results of free U<sup>4+</sup> ion obtained from DFT calculation using the hybrid B3LYP functional, showing the multiplet energies of the configuration  $4f^{13}5f^26d^1$  (in red) and intensity of the  $5f^2 \rightarrow 4f^{13}5f^26d^1$  transitions, *i.e.* oscillator strengths (in black) and Lorentzian broadening (in grey) (a) and the deconvolution of the intensity as function of final electronic states with J = 3 (in magenta), J = 4 (in blue) and J = 5 (in green) values (b). In the ordinates, the intensity plots are given in arbitrary unit.



**Fig. S3** Calculated radial functions of the Kohn-Sham orbitals with dominant uranium 4f (a) character obtained for the configuration  $4f^{13}5f^26d^1$  in the free ion (dashed curve) and in  $(UO_8)^{12}$  (solid curve). They are needed for the evaluation of the Slater-Condon integrals (see the text for details). The changes of the radial functions from free ion to molecular cluster are highlighted.

	-	
$E_i - E_0$	Ι	Assignment
		$ 4f^{13}5f^{2}6d^{1}, J=5>$
387.526	0.0032	$15.79 \% {}^{5}\text{H} + 16.76 \% {}^{3}\text{I} + \dots$
387.785	0.0014	$11.77 \% {}^{5}\text{G} + 12.90 \% {}^{5}\text{H} + \dots$
387.908	0.0014	
387.935	0.0102	$10.84 \% {}^{1}H +$
388.075	0.0014	$17.68 \% {}^{5}\text{G} + 10.19 \% {}^{5}\text{H} + \dots$
388.237	0.0071	$17.00 \% {}^{5}F + 12.44 \% {}^{3}G + \dots$
388.538	0.0018	$15.39 \% {}^{5}F + 12.49 \% {}^{3}G + \dots$
388.614	0.0135	
388.657	0.0210	$13.48 \% {}^{5}F + 13.05 {}^{5}G \% + \dots$
388.730	0.0117	
388.750	0.0476	
388.787	0.0038	
388.931	0.0025	
388.976	0.0404	$18.12 \% {}^{3}\text{I} + \dots$
389.079	0.0012	15.40 % <sup>5</sup> G +
389.180	0.0100	$12.15 \% {}^{5}F + 11.05 \% {}^{3}I + \dots$
389.294	0.0069	12.49 % <sup>5</sup> H +
389.358	0.0094	
389.494	0.0074	$11.73 \% {}^{3}\text{H} + \dots$
389.549	0.0030	12.49 % <sup>5</sup> G +
389.817	0.0030	$10.36\%^{3}G + \dots$
390.015	0.0010	
390.087	0.0015	
390.238	0.0013	
390.619	0.0020	
390.687	0.0023	
397.424	0.0145	$18.69 \% {}^{5}\text{K} + 28.54 \% {}^{5}\text{I} + \dots$
397.868	0.0111	22.23 % ${}^{5}$ K + 16.13 % ${}^{5}$ K + 16.53 % ${}^{3}$ I + 16.32 % ${}^{3}$ I +
398,196	0.1073	$11.29 \% {}^{3}\text{I} + 27.78 \% {}^{5}\text{K} + 21.47 \% {}^{3}\text{I} + \dots$
398.324	0.0012	$10.13 \% {}^{3}\text{G} + 13.87 \% {}^{5}\text{K} + 10.46 \% {}^{1}\text{H} + 13.72 \% {}^{5}\text{K} + \dots$
398.472	0.0026	$10.31 \% {}^{5}I + 12.48 \% {}^{3}I + \dots$
398.880	0.0156	$16.19\% ^{5}I + \dots$
398.893	0.0035	$25.72 \% {}^{5}K + 11.49 \% {}^{3}I + \dots$
398.953	0.0023	$18.70 \% {}^{5}K + \dots$
399.123	0.0115	$14.81 \% {}^{5}I + 13.26 \% {}^{5}K + \dots$
399.599	0.0023	13.69 % <sup>5</sup> I +
401.242	0.0011	11.91 % <sup>1</sup> H +
		$ 4f^{13}5f^{2}6d^{1}, J=4>$
387.585	0.0049	$13.92 \% {}^{3}\text{G} + 19.49 \% {}^{5}\text{G} + 12.87 \% {}^{3}\text{H} + \dots$
387.881	0.0026	12.45 % <sup>5</sup> H +
388.096	0.0017	$13.64 \% {}^{3}H + \dots$
388.186	0.0129	$17.54 \% {}^{3}\text{H} + \dots$
388.308	0.0097	$11.27 \% {}^{5}D + \dots$
388.498	0.0089	$15.67 \% {}^{3}H + \dots$
388.555	0.0030	
388.632	0.0021	$22.36 \% {}^{3}\text{G} + \dots$
388.922	0.0023	
388.981	0.0144	$14.49 \% {}^{3}F + \dots$
389.104	0.0172	
389.157	0.0087	
389.257	0.0128	
389.288	0.0052	
389.402	0.0011	
389.429	0.0076	
389.469	0.0083	$14.44 \% {}^{3}H + \dots$
389.558	0.0048	$11.71 \% {}^{3}F + \dots$
389.658	0.0062	

**Table S1**. Calculated excitation energies  $(E_i - E_0)$ , oscillator strengths (*I*) and assignment of the multiplet terms with nonzero transition probabilities obtained in the intra-atomic  $5f^2 \rightarrow 4f^{13}5f^26d^1$  electron transitions in U<sup>4+</sup>.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	389 678	0.0172	12 00 % <sup>5</sup> D +
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	390.007	0.0080	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	390.256	0.0035	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	390.230	0.0033	12 22 0/ <sup>3</sup> U +
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	390.413	0.0021	$12.25 \times 10^{-11} \text{ m}^{-1}$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	390.893	0.0023	$21.16 \ /0 \ 11 + \dots$ 11 82 9/ <sup>5</sup> I +
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	393.010	0.0034	$11.62 \ 70 \ 1 \pm \dots$ 18.88 0/ $51 \pm 20.58 \ 0/ \ ^{3}11 \pm 15.24 \ 0/ \ ^{5}11 \pm$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	397.091	0.0555	18.88 $\%$ 1 + 20.38 $\%$ 1 + 13.24 $\%$ 1 +
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	398.184	0.0182	12.15 % 1 + 12.27 % H +
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	398.502	0.0029	10.26 % F + $15.84 %$ H + $13.39 %$ G +
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	398.780	0.0029	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	398.886	0.0616	$19.51 \% 1 + 11.49 \% 1 + 11.71 \% H + \dots$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	398.963	0.0068	18.92%1+
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	399.003	0.0013	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	399.742	0.0011	10.52% H +
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	399.999	0.0027	11.67 % '1+
$ 4^{12}5^{16}6^{17}, d = 3^{16}$ $ 37,330 = 0.0114 = 12.65 \%^{16} + 12.25 6\%^{16} + 11.02 \%^{16} + 15.69 \%^{16} + \\ 1387,445 = 0.0069 = 17.29 \%^{16} + 10.41 \%^{16} + 12.53 \%^{16} + \\ 1387,928 = 0.0010 = 11.75 \%^{16} + \\ 1388,190 = 0.0015 = 11.75 \%^{16} + \\ 1388,613 = 0.0137 = 10.43 \%^{16} - 4 \\ 1388,722 = 0.0073 = 18.84 \%^{16} T + \\ 1388,884 = 0.0067 = 13.40 \%^{16} + \\ 1388,884 = 0.0067 = 13.40 \%^{16} + \\ 1388,903 = 0.0079 = 10.77 \%^{16} - 4 \\ 1389,003 = 0.0079 = 10.77 \%^{16} - 4 \\ 1389,003 = 0.0079 = 10.77 \%^{16} - 4 \\ 1389,153 = 0.0014 = 13.27 \%^{17} + \\ 1389,153 = 0.0014 = 13.27 \%^{17} + \\ 1389,153 = 0.0014 = 13.27 \%^{17} + \\ 1389,154 = 0.0012 = 11.86 \%^{17} D + \\ 1389,434 = 0.0055 = 11.86 \%^{17} D + \\ 1389,777 = 0.0013 = 11.86 \%^{17} D + \\ 1393,639 = 0.0011 = 11.86 \%^{17} D + \\ 1393,639 = 0.0011 = 11.86 \%^{17} D + \\ 1393,639 = 0.0012 = 11.86 \%^{17} D + \\ 1393,635 = 0.0012 = 11.68 \%^{17} D + \\ 1393,777 = 0.013 = 19.25 \%^{17} + 1.03.65 \%^{17} + 11.90 \%^{17} F + \\ 1393,777 = 0.014 = 19.25 \%^{17} H + 10.06 \%^{17} F + \\ 1393,789 = 0.0016 = 14.57 \%^{17} H + 10.36 \%^{17} F + 1 \\ 1393,167 = 0.025 = 19.25 \%^{11} H + 30.66 \%^{16} G + \\ 1393,780 = 0.0166 = 14.57 \%^{17} H + 10.31 \%^{17} G + \\ 1398,150 = 0.0032 = 12.83 \%^{17} H + 10.31 \%^{17} G + \\ 1398,150 = 0.0032 = 12.83 \%^{17} H + 10.08 \%^{17} H + \\ 1398,150 = 0.0032 = 12.83 \%^{17} H + 10.08 \%^{17} H + \\ 1398,150 = 0.0012 = 10.60 \%^{17} G + \\ 1398,150 = 0.0012 = 10.60 \%^{17} H + \\ 1398,150 = 0.0013 = 12.83 \%^{17} H + 10.31 \%^{17} H + \\ 1398,150 = 0.0014 = 10.70 \%^{17} H + \\ 1398,454 = 0.0191 = 10.70 \%^{17} H + \\ 1398,454 = 0.0191 = 10.70 \%^{17} H + \\ 1398,454 = 0.0191 = 10.70 \%^{17} H + \\ 1398,454 = 0.0191 = 10.70 \%^{17} H + \\ 1398,454 = 0.0191 = 10.70 \%^{17} H + \\ 1398,454 = 0.0191 = 10.70 \%^{17} H + \\ 1398,454 = 0.0191 = 10.70 \%^{17} H + \\ 1398,457 = 0.0122 = 0.975 \%^{17} H + \\ 1398,457 = 0.012 = 0.975 \%^{$	410.425	0.0033	19.95 % 'G + 69.66 % 'H +
387.30       0.0114       12.65 % <sup>1</sup> C + 11.02 % <sup>1</sup> C + 15.60 % <sup>1</sup> C +         387.455       0.0000       17.29 % <sup>1</sup> F + 10.41 % <sup>1</sup> C + 12.53 % <sup>1</sup> F +         387.965       0.0010       11.75 % <sup>1</sup> D +         388.190       0.0015       11.75 % <sup>1</sup> D +         388.568       0.0242       17.60 % <sup>1</sup> C 4         388.702       0.0073       10.43 % <sup>1</sup> G +         388.789       0.0015       18.84 % <sup>1</sup> F +         388.879       0.0015       18.84 % <sup>1</sup> F +         388.923       0.0073       10.77 % <sup>1</sup> G +         389.075       0.0011       13.20 % <sup>1</sup> D +         389.075       0.0014       13.27 % <sup>1</sup> D +         389.13       0.0014       13.27 % <sup>1</sup> D +         389.13       0.0012       11.86 % <sup>1</sup> D +         389.51       0.0012       11.86 % <sup>1</sup> D +         389.524       0.0029       13.366 % <sup>1</sup> C + 11.09 % <sup>1</sup> F +         389.51       0.0012       11.68 % <sup>1</sup> D +         389.525       0.0020       18.36 % <sup>1</sup> C + 11.09 % <sup>1</sup> F +         393.451       0.0060       17.34 % <sup>1</sup> D +         393.559       0.0020       18.36 % <sup>1</sup> C + 11.03 % <sup>1</sup> C + 11.09 % <sup>1</sup> C +         393.451       0.0060			$ 4f^{45}5f^{2}6d^{1}, J=3>$
337,4450.0012 $1.433 \ \%^{1}F +$ 337,5550.006917.29 \ \%^{1}F + 10.41 \ \% \ G + 12.33 \ \%^{1}F +338,75280.001511.75 \ \%^{1}D +338,81900.001511.75 \ \%^{1}D +338,86130.013710.43 \ \%^{1}G +338,86130.013710.43 \ \%^{1}G +338,87290.007313.40 \ \%^{1}D +338,82330.007313.40 \ \%^{1}D +388,9030.007910.77 \ \%^{1}G +389,0030.007910.77 \ \%^{1}G +389,0050.001113.27 \ \%^{1}F +389,1530.001413.27 \ \%^{1}F +389,3710.003511.86 \ \%^{2}D +389,6390.001111.86 \ \%^{2}D +389,7740.0013389,9770.0013389,9770.0014389,9770.0013389,9770.0014389,9770.0013389,9770.0014393,5110.006017.34 \ \%^{1}D +393,6050.0012393,6050.0012393,6050.0012393,7270.0018397,1670.0205393,7270.0018393,7270.0018393,7270.0018393,7270.0018393,7450.0072398,7560.0015398,7560.0015398,7560.0015398,7560.0015399,7560.0015399,7560.0015399,7560.0015<	387.330	0.0114	12.65 % <sup>5</sup> H + 22.26 % <sup>5</sup> G + 22.56 % <sup>5</sup> G + 11.02 % <sup>3</sup> G + 15.69 % <sup>3</sup> G +
337,5650.0009 $17.29 \%^{2}F + 1.0.41 \%^{2}G + 12.33 \%^{2}F +337,2650.001511.75 \%^{2}D +338,1900.001511.75 \%^{2}D +338,6880.024217.60 \%^{2}G +338,7020.007310.43 \%^{2}D +338,7390.001518.84 \%^{2}P +338,9230.007310.77 \%^{2}G +389,0030.007910.77 \%^{2}G +389,0050.0011389,0750.0011389,3710.0025389,3710.0012389,6390.0012389,6390.0011389,7770.0013389,7770.0013389,7740.0012390,8410.0029390,0140.0012390,8410.0012393,8510.0001393,3550.0012393,6550.0012393,6560.0012393,6570.0012393,6580.0012393,6590.0012393,6550.0012393,6550.0023393,6550.0023393,6550.0023393,6550.0015398,7660.015399,4760.019399,4760.019399,4760.019399,4760.019399,4760.019399,4760.019399,4760.019399,4760.019399,4760.01240,8471.079 \%^{2}H +399,4760.019399,476$	387.445	0.0012	$14.83 \% {}^{3}F + \dots$
337,9280.0010338,1900.0015 $11.75 \ \%^{1}D +$ 338,1900.0015 $11.75 \ \%^{1}D +$ 338,7020.0073338,703 $10.43 \ \%^{1}C +$ 338,7040.0015 $18.84 \ \%^{1}F +$ 338,7050.0073389,0030.0079 $10.77 \ \%^{1}G +$ 389,0030.0079 $10.77 \ \%^{1}G +$ 389,0150.0011389,0250.0014 $13.27 \ \%^{1}F +$ 389,3220.0065389,3220.0073389,710.0055389,4130.0055389,4130.0055389,5110.0012389,6390.0011389,7740.0013389,7740.0013389,7750.0014389,9240.0029390,0140.0012390,8110.0067393,4510.006017,34 \ \%^{1}D +393,6550.0012393,6650.0012393,6650.0012393,6760.0023393,6760.0015398,3760.015398,3760.015398,3760.012398,3760.015398,3760.015399,4760.019399,4760.019399,4760.019399,4760.019399,4760.019399,4760.015399,4760.012399,4760.012399,4760.014399,4760.012399,	387.565	0.0069	$17.29 \% {}^{5}F + 10.41 \% {}^{3}G + 12.53 \% {}^{3}F + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	387.928	0.0010	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	388.190	0.0015	$11.75 \% {}^{5}D + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	388.568	0.0242	$17.60 \% {}^{3}\text{G} + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	388.613	0.0137	$10.43 \% {}^{3}\text{G} + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	388.702	0.0073	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	388.789	0.0015	$18.84 \% {}^{3}F + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	388.884	0.0067	13.40 % <sup>s</sup> D +
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	388.923	0.0073	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.003	0.0079	$10.77 \% {}^{3}G + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.075	0.0011	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.153	0.0014	13.27 % <sup>1</sup> F +
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.322	0.0065	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.329	0.0074	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.371	0.0035	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.443	0.0055	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.511	0.0012	$11.86 \% ^{3}D + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.639	0.0011	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.724	0.0019	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.777	0.0013	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.907	0.0014	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	389.924	0.0029	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	390.014	0.0012	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	390.881	0.0010	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	393.381	0.0067	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	393.451	0.0060	17.34 % <sup>3</sup> D +
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	393.559	0.0020	$18.36 \% {}^{3}F + 10.36 \% {}^{3}F + 11.90 \% {}^{1}F +$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	393.605	0.0012	$11.68\%^{3}D + \dots$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	393.727	0.0018	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	397 167	0.0205	19 92 % <sup>5</sup> H + 36 06 % <sup>3</sup> G +
398.1500.0023 $12.83 \ \%^5 G + 12.04 \ \%^3 F +$ 398.3050.0072 $16.00 \ \%^3 G + 10.84 \ \%^1 F + 10.08 \ \%^1 F +$ 398.4540.0191 $10.42 \ \%^3 F + 15.57 \ \%^3 G +$ 398.7300.0126398.7560.0015399.0650.0014399.4760.001910.70 \ \%^5 H +399.8710.002617.58 \ \%^5 H +410.8470.010269.75 \ \%^3 G + 17.34 \ \%^1 F +	397 689	0.0166	$1457\%^{5}H + 1031\%^{3}G + 1139\%^{3}G +$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	398 150	0.0023	$12.83\%^{5}G + 12.04\%^{3}F +$
$398.454$ $0.0191$ $10.42 \% {}^{3}F + 15.57 \% {}^{3}G +$ $398.730$ $0.0126$ $398.756$ $0.0015$ $399.065$ $0.0014$ $399.476$ $0.0019$ $399.640$ $0.0044$ $399.871$ $0.0026$ $17.58 \% {}^{5}H +$ $410.847$ $0.0102$ $69.75 \% {}^{3}G + 17.34 \% {}^{1}F +$	398.305	0.0072	$16.00 \% {}^{3}\text{G} + 10.84 \% {}^{1}\text{F} + 10.08 \% {}^{1}\text{F} +$
398.730 $0.0126$ $398.756$ $0.0015$ $399.655$ $0.0014$ $399.476$ $0.0019$ $399.640$ $0.0044$ $399.871$ $0.0026$ $410.847$ $0.0102$	398 454	0.0191	$10.42 \% {}^{3}F + 15.57 \% {}^{3}G +$
398.756       0.0015         399.065       0.0014         399.476       0.0019         399.640       0.0044         399.871       0.0026         410.847       0.0102         69.75 % <sup>3</sup> G + 17.34 % <sup>1</sup> F +	398 730	0.0126	10.12/01/10.07/000/11
399.065       0.0014         399.476       0.0019         399.640       0.0044         399.871       0.0026         410.847       0.0102         69.75 % <sup>3</sup> G + 17.34 % <sup>1</sup> F +	398 756	0.0120	
399.476       0.0019       10.70 % <sup>5</sup> H +         399.640       0.0044       10.79 % <sup>5</sup> H + 13.74 % <sup>5</sup> G +         399.871       0.0026       17.58 % <sup>5</sup> H +         410.847       0.0102       69.75 % <sup>3</sup> G + 17.34 % <sup>1</sup> F +	300.065	0.0013	
$399.640$ $0.0044$ $10.79 \% {}^{5}H + 13.74 \% {}^{5}G +$ $399.871$ $0.0026$ $17.58 \% {}^{5}H +$ $410.847$ $0.0102$ $69.75 \% {}^{3}G + 17.34 \% {}^{1}F +$	300 176	0.0014	10 70 % <sup>5</sup> H +
$399.871$ $0.0026$ $17.58 \% {}^{5}H + \dots$ $410.847$ $0.0102$ $69.75 \% {}^{3}G + 17.34 \% {}^{1}F + \dots$	300 640	0.0019	$10.70\% 11^{+}$ $10.70\% ^{5}$ H + 13.74% $^{5}$ C +
$410.847    0.0102    69.75 \% {}^{3}G + 17.34 \% {}^{1}F + \dots$	300 971	0.0044	$10.77 \times 10^{-11} \times 15.74 \times 10^{-7} \times 10^{-7}$
+10.047     0.0102     09.73 % G+17.34 % F+	J77.0/1 110.017	0.0020	$\frac{1}{30} \frac{1}{30} \frac{1}{10} \frac$
	410.04/	0.0102	U7./J 70 U T 1/.34 70 Γ T