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Supporting Information: Relativistic effects on atomic orbitals across the periodic table: Insights from spin-separated Dirac–Coulomb–Breit Hamiltonian†

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S1 Orbital energies

In this section we report orbital energies and orbital fine structure for all atoms investigated in this work. Characterizations of the magnitude shift upon Hamiltonian substitution are presented in the main text for selected atoms. The one-electron exact 2-component (X2C), Dirac–Coulomb (DC), Dirac–Coulomb–Gaunt (DCG), and Dirac–Coulomb-Breit (DCB) Hamiltonians are explored along with their scalar-relativistic counterparts (denoted with a preceding "sr").

S1.1 s-block atoms

Table S1 Orbital energies (in eV) of Be atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−128.797	−128.805	−128.790	−128.790
$2s$	−8.417	−8.417	−8.417	−8.417

Table S2 Orbital energies (in eV) of Be atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−128.797	−128.805	−128.790	−128.790
$2s_{1/2}$	−8.417	−8.417	−8.417	−8.417

Table S3 Orbital energies (in eV) of Mg atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−1336.530	−1336.805	−1336.231	−1336.240
$2s$	−102.848	−102.863	−102.847	−102.846
$2p$	−62.056	−62.058	−62.037	−62.040
$3s$	−6.896	−6.897	−6.896	−6.896

Table S4 Orbital energies (in eV) of Mg atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−1336.530	−1336.805	−1336.230	−1336.240
$2s_{1/2}$	−102.848	−102.863	−102.847	−102.846
$2p_{1/2}$	−62.264	−62.268	−62.234	−62.237
$2p_{3/2}$	−61.953	−61.953	−61.939	−61.942
$3s_{1/2}$	−6.896	−6.897	−6.896	−6.896

Table S5 Orbital fine structure (in eV) of Mg atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	0.312	0.315	0.295	0.295

Table S6 Orbital energies (in eV) of Ca atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−4084.770	−4086.178	−4082.890	−4083.037
$2s$	−461.603	−461.709	−461.545	−461.543
$2p$	−371.088	−371.125	−370.877	−370.910
$3s$	−61.544	−61.554	−61.544	−61.543
$3p$	−36.433	−36.433	−36.420	−36.422
$4s$	−5.341	−5.342	−5.341	−5.341

Table S7 Orbital energies (in eV) of Ca atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−4084.765	−4086.165	−4082.877	−4083.024
$2s_{1/2}$	−461.602	−461.707	−461.543	−461.541
$2p_{1/2}$	−373.615	−373.657	−373.324	−373.357
$2p_{3/2}$	−369.833	−369.870	−369.664	−369.697
$3s_{1/2}$	−61.544	−61.553	−61.543	−61.543
$3p_{1/2}$	−36.714	−36.714	−36.690	−36.693
$3p_{3/2}$	−36.294	−36.295	−36.286	−36.288
$4s_{1/2}$	−5.342	−5.342	−5.341	−5.341

Table S8 Orbital fine structure (in eV) of Ca atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	3.782	3.787	3.660	3.660
$3p_{3/2}-3p_{1/2}$	0.421	0.419	0.405	0.405

Table S9 Orbital energies (in eV) of Sr atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−16197.497	−16208.164	−16180.791	−16182.558
$2s$	−2261.495	−2262.562	−2260.428	−2260.520
$2p$	−2004.109	−2004.633	−2001.410	−2001.851
$3s$	−379.721	−379.878	−379.654	−379.658
$3p$	−293.974	−294.027	−293.670	−293.725
$3d$	−152.029	−152.018	−152.027	−152.022
$4s$	−53.020	−53.035	−53.020	−53.019
$4p$	−29.799	−29.799	−29.778	−29.782
$5s$	−4.931	−4.932	−4.932	−4.931

Table S10 Orbital energies (in eV) of Sr atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−16197.269	−16207.751	−16180.380	−16182.123
$2s_{1/2}$	−2261.444	−2262.488	−2260.359	−2260.453
$2p_{1/2}$	−2050.463	−2051.087	−2047.081	−2047.515
$2p_{3/2}$	−1981.548	−1982.144	−1979.332	−1979.765
$3s_{1/2}$	−379.707	−379.858	−379.635	−379.639
$3p_{1/2}$	−301.421	−301.450	−300.965	−301.020
$3p_{3/2}$	−290.346	−290.426	−290.136	−290.190
$3d_{3/2}$	−153.160	−153.161	−153.119	−153.115
$3d_{5/2}$	−151.269	−151.245	−151.285	−151.282
$4s_{1/2}$	−53.018	−53.032	−53.017	−53.016
$4p_{1/2}$	−30.658	−30.652	−30.616	−30.620
$4p_{3/2}$	−29.382	−29.386	−29.372	−29.376
$5s_{1/2}$	−4.932	−4.932	−4.932	−4.932

Table S11 Orbital fine structure (in eV) of Sr atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	68.915	68.943	67.750	67.751
$3p_{3/2}-3p_{1/2}$	11.075	11.023	10.830	10.830
$3d_{5/2}-3d_{3/2}$	1.891	1.916	1.834	1.834
$4p_{3/2}-4p_{1/2}$	1.276	1.265	1.244	1.243

Table S12 Orbital energies (in eV) of Ba atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−37622.770	−37659.608	−37561.576	−37568.777
$2s$	−6053.008	−6057.343	−6047.908	−6048.541
$2p$	−5425.832	−5427.987	−5414.331	−5416.253
$3s$	−1323.308	−1324.106	−1322.729	−1322.797
$3p$	−1116.888	−1117.218	−1115.154	−1115.453
$3d$	−814.891	−814.960	−814.392	−814.443
$4s$	−279.036	−279.185	−278.984	−278.991
$4p$	−209.509	−209.549	−209.237	−209.289
$4d$	−104.884	−104.868	−104.894	−104.891
$5s$	−43.626	−43.645	−43.629	−43.628
$5p$	−24.472	−24.472	−24.447	−24.452
$6s$	−4.438	−4.439	−4.438	−4.438

Table S13 Orbital energies (in eV) of Ba atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−37620.577	−37656.055	−37558.119	−37565.077
$2s_{1/2}$	−6052.456	−6056.639	−6047.236	−6047.885
$2p_{1/2}$	−5686.463	−5689.572	−5672.793	−5674.656
$2p_{3/2}$	−5303.768	−5306.495	−5294.574	−5296.430
$3s_{1/2}$	−1323.123	−1323.878	−1322.511	−1322.582
$3p_{1/2}$	−1168.579	−1168.907	−1166.244	−1166.531
$3p_{3/2}$	−1092.508	−1093.006	−1091.278	−1091.565
$3d_{3/2}$	−824.358	−824.446	−823.620	−823.675
$3d_{5/2}$	−808.462	−808.502	−808.084	−808.137
$4s_{1/2}$	−278.978	−279.115	−278.915	−278.923
$4p_{1/2}$	−220.367	−220.388	−219.949	−219.998
$4p_{3/2}$	−204.366	−204.445	−204.202	−204.252
$4d_{3/2}$	−106.525	−106.493	−106.473	−106.470
$4d_{5/2}$	−103.759	−103.746	−103.798	−103.795
$5s_{1/2}$	−43.619	−43.635	−43.618	−43.618
$5p_{1/2}$	−26.032	−26.026	−25.982	−25.987
$5p_{3/2}$	−23.741	−23.747	−23.731	−23.735
$6s_{1/2}$	−4.439	−4.440	−4.440	−4.440

Table S14 Orbital fine structure (in eV) of Ba atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	382.695	383.077	378.219	378.225
$3p_{3/2}-3p_{1/2}$	76.071	75.901	74.966	74.967
$3d_{5/2}-3d_{3/2}$	15.897	15.945	15.536	15.537
$4p_{3/2}-4p_{1/2}$	16.001	15.944	15.746	15.747
$4d_{5/2}-4d_{3/2}$	2.766	2.747	2.675	2.675
$5p_{3/2}-5p_{1/2}$	2.291	2.279	2.252	2.251

Table S15 Orbital energies (in eV) of Ra atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−104526.271	−104704.638	−104256.442	−104292.336
$2s$	−19377.670	−19404.613	−19351.329	−19355.882
$2p$	−16439.792	−16449.845	−16379.698	−16389.702
$3s$	−4887.622	−4893.543	−4883.216	−4884.128
$3p$	−4047.041	−4049.194	−4035.729	−4037.679
$3d$	−3213.938	−3214.749	−3208.569	−3209.333
$4s$	−1243.038	−1244.485	−1242.265	−1242.472
$4p$	−962.204	−962.639	−959.830	−960.268
$4d$	−644.282	−644.351	−643.605	−643.706
$4f$	−304.863	−304.753	−305.178	−305.093
$5s$	−272.295	−272.586	−272.221	−272.249
$5p$	−185.218	−185.268	−184.833	−184.906
$5d$	−81.512	−81.485	−81.523	−81.519
$6s$	−44.212	−44.255	−44.221	−44.221
$6p$	−21.991	−21.988	−21.949	−21.957
$7s$	−4.503	−4.506	−4.506	−4.505

Table S16 Orbital energies (in eV) of Ra atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−104488.918	−104650.988	−104204.093	−104236.512
$2s_{1/2}$	−19367.376	−19392.631	−19339.449	−19344.232
$2p_{1/2}$	−18613.651	−18642.438	−18551.943	−18561.097
$2p_{3/2}$	−15547.651	−15563.128	−15504.653	−15513.840
$3s_{1/2}$	−4884.101	−4889.547	−4879.309	−4880.265
$3p_{1/2}$	−4545.325	−4550.679	−4533.013	−4534.781
$3p_{3/2}$	−3838.407	−3841.852	−3830.913	−3832.687
$3d_{3/2}$	−3300.605	−3301.170	−3293.409	−3294.220
$3d_{5/2}$	−3154.338	−3155.405	−3150.069	−3150.849
$4s_{1/2}$	−1241.811	−1243.095	−1240.911	−1241.118
$4p_{1/2}$	−1090.551	−1091.612	−1087.671	−1088.080
$4p_{3/2}$	−908.019	−908.816	−906.662	−907.051
$4d_{3/2}$	−664.663	−664.470	−663.351	−663.465
$4d_{5/2}$	−630.022	−630.228	−629.673	−629.781
$4f_{5/2}$	−309.231	−309.006	−309.267	−309.189
$4f_{7/2}$	−300.748	−300.587	−301.100	−301.022
$5s_{1/2}$	−271.928	−272.167	−271.811	−271.834
$5p_{1/2}$	−213.308	−213.443	−212.754	−212.820
$5p_{3/2}$	−173.301	−173.426	−173.128	−173.192
$5d_{3/2}$	−84.951	−84.836	−84.810	−84.808
$5d_{5/2}$	−78.987	−78.988	−79.053	−79.051
$6s_{1/2}$	−44.179	−44.210	−44.174	−44.175
$6p_{1/2}$	−26.497	−26.503	−26.424	−26.431
$6p_{3/2}$	−20.146	−20.154	−20.134	−20.141
$7s_{1/2}$	−4.522	−4.523	−4.522	−4.522

S1.2 p-block atoms

Table S17 Orbital fine structure (in eV) of Ra atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	3066.000	3079.310	3047.290	3047.258
$3p_{3/2}-3p_{1/2}$	706.919	708.827	702.100	702.095
$3d_{5/2}-3d_{3/2}$	146.267	145.765	143.340	143.370
$4p_{3/2}-4p_{1/2}$	182.532	182.796	181.010	181.030
$4d_{5/2}-4d_{3/2}$	34.641	34.242	33.678	33.684
$4f_{7/2}-4f_{5/2}$	8.483	8.419	8.167	8.167
$5p_{3/2}-5p_{1/2}$	40.007	40.017	39.626	39.628
$5d_{5/2}-5d_{3/2}$	5.964	5.849	5.758	5.757
$6p_{3/2}-6p_{1/2}$	6.351	6.350	6.290	6.290

Table S18 Orbital energies (in eV) of Ne atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−892.855	−893.008	−892.702	−892.703
$2s$	−52.670	−52.677	−52.672	−52.671
$2p$	−23.123	−23.123	−23.118	−23.119

Table S19 Orbital energies (in eV) of Ne atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−892.855	−893.008	−892.702	−892.703
$2s_{1/2}$	−52.670	−52.677	−52.672	−52.671
$2p_{1/2}$	−23.205	−23.206	−23.194	−23.195
$2p_{3/2}$	−23.083	−23.082	−23.080	−23.081

Table S20 Orbital fine structure (in eV) of Ne atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	0.122	0.124	0.114	0.114

Table S21 Orbital energies (in eV) of Ar atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−3240.600	−3241.606	−3239.310	−3239.400
$2s$	−337.665	−337.737	−337.636	−337.633
$2p$	−260.533	−260.555	−260.400	−260.421
$3s$	−35.004	−35.009	−35.006	−35.005
$3p$	−16.063	−16.063	−16.059	−16.060

Table S22 Orbital energies (in eV) of Ar atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−3240.597	−3241.599	−3239.302	−3239.393
$2s_{1/2}$	−337.665	−337.736	−337.635	−337.632
$2p_{1/2}$	−262.071	−262.098	−261.886	−261.906
$2p_{3/2}$	−259.767	−259.788	−259.663	−259.684
$3s_{1/2}$	−35.004	−35.009	−35.006	−35.005
$3p_{1/2}$	−16.202	−16.201	−16.191	−16.192
$3p_{3/2}$	−15.995	−15.995	−15.993	−15.994

Table S23 Orbital fine structure (in eV) of Ar atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	2.304	2.310	2.222	2.222
$3p_{3/2}-3p_{1/2}$	0.207	0.206	0.198	0.198

Table S24 Orbital energies (in eV) of Kr atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−14404.773	−14413.766	−14390.862	−14392.306
$2s$	−1960.561	−1961.444	−1959.715	−1959.782
$2p$	−1728.355	−1728.784	−1726.157	−1726.515
$3s$	−305.320	−305.446	−305.276	−305.277
$3p$	−228.895	−228.936	−228.663	−228.705
$3d$	−101.978	−101.968	−101.992	−101.986
$4s$	−32.310	−32.321	−32.316	−32.314
$4p$	−14.236	−14.236	−14.229	−14.230

Table S25 Orbital energies (in eV) of Kr atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−14404.608	−14413.460	−14390.556	−14391.982
$2s_{1/2}$	−1960.525	−1961.391	−1959.664	−1959.733
$2p_{1/2}$	−1764.826	−1765.333	−1762.056	−1762.409
$2p_{3/2}$	−1710.549	−1711.030	−1708.742	−1709.095
$3s_{1/2}$	−305.311	−305.433	−305.263	−305.264
$3p_{1/2}$	−234.538	−234.559	−234.183	−234.225
$3p_{3/2}$	−226.140	−226.202	−225.982	−226.024
$3d_{3/2}$	−102.796	−102.795	−102.779	−102.774
$3d_{5/2}$	−101.432	−101.411	−101.459	−101.454
$4s_{1/2}$	−32.310	−32.320	−32.315	−32.313
$4p_{1/2}$	−14.740	−14.735	−14.718	−14.720
$4p_{3/2}$	−13.993	−13.996	−13.993	−13.994

Table S26 Orbital fine structure (in eV) of Kr atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	54.277	54.303	53.314	53.314
$3p_{3/2}-3p_{1/2}$	8.397	8.357	8.201	8.202
$3d_{5/2}-3d_{3/2}$	1.364	1.384	1.319	1.319
$4p_{3/2}-4p_{1/2}$	0.747	0.739	0.726	0.726

Table S27 Orbital energies (in eV) of Xe atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−34726.071	−34758.796	−34671.891	−34678.206
$2s$	−5506.124	−5509.915	−5501.707	−5502.241
$2p$	−4937.432	−4939.329	−4927.382	−4929.060
$3s$	−1169.864	−1170.552	−1169.387	−1169.440
$3p$	−981.295	−981.578	−979.818	−980.073
$3d$	−700.200	−700.254	−699.806	−699.844
$4s$	−229.316	−229.440	−229.282	−229.286
$4p$	−166.867	−166.900	−166.653	−166.694
$4d$	−72.540	−72.527	−72.563	−72.558
$5s$	−27.476	−27.490	−27.484	−27.482
$5p$	−12.420	−12.420	−12.410	−12.412

Table S28 Orbital energies (in eV) of Xe atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−34724.306	−34755.906	−34669.075	−34675.194
$2s_{1/2}$	−5505.687	−5509.350	−5501.169	−5501.716
$2p_{1/2}$	−5158.790	−5161.449	−5146.774	−5148.403
$2p_{3/2}$	−4833.217	−4835.587	−4825.148	−4826.772
$3s_{1/2}$	−1169.721	−1170.373	−1169.216	−1169.272
$3p_{1/2}$	−1024.513	−1024.780	−1022.500	−1022.746
$3p_{3/2}$	−960.823	−961.249	−959.776	−960.022
$3d_{3/2}$	−708.057	−708.132	−707.460	−707.502
$3d_{5/2}$	−694.876	−694.900	−694.583	−694.623
$4s_{1/2}$	−229.275	−229.390	−229.232	−229.236
$4p_{1/2}$	−175.568	−175.581	−175.227	−175.267
$4p_{3/2}$	−162.735	−162.800	−162.610	−162.649
$4d_{3/2}$	−73.806	−73.779	−73.777	−73.773
$4d_{5/2}$	−71.679	−71.668	−71.725	−71.720
$5s_{1/2}$	−27.476	−27.487	−27.481	−27.479
$5p_{1/2}$	−13.409	−13.404	−13.381	−13.383
$5p_{3/2}$	−11.964	−11.968	−11.963	−11.965

Table S29 Orbital fine structure (in eV) of Xe atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	325.572	325.862	321.626	321.631
$3p_{3/2}-3p_{1/2}$	63.690	63.530	62.724	62.725
$3d_{5/2}-3d_{3/2}$	13.181	13.232	12.878	12.879
$4p_{3/2}-4p_{1/2}$	12.832	12.781	12.617	12.618
$4d_{5/2}-4d_{3/2}$	2.127	2.111	2.053	2.053
$5p_{3/2}-5p_{1/2}$	1.445	1.436	1.418	1.418

Table S30 Orbital energies (in eV) of Rn atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−98964.963	−99128.144	−98714.386	−98747.417
$2s$	−18185.203	−18209.470	−18160.834	−18164.946
$2p$	−15514.818	−15524.140	−15459.618	−15468.816
$3s$	−4537.824	−4543.126	−4533.810	−4534.614
$3p$	−3768.370	−3770.340	−3758.065	−3759.842
$3d$	−2984.711	−2985.454	−2979.873	−2980.559
$4s$	−1124.059	−1125.343	−1123.376	−1123.554
$4p$	−866.787	−867.182	−864.662	−865.056
$4d$	−568.502	−568.566	−567.921	−568.009
$4f$	−246.576	−246.477	−246.893	−246.812
$5s$	−228.886	−229.137	−228.836	−228.857
$5p$	−150.755	−150.799	−150.440	−150.500
$5d$	−56.878	−56.857	−56.908	−56.901
$6s$	−29.117	−29.151	−29.135	−29.133
$6p$	−11.639	−11.639	−11.622	−11.625

Table S31 Orbital energies (in eV) of Rn atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−98933.079	−99082.026	−98669.447	−98699.452
$2s_{1/2}$	−18176.495	−18199.291	−18150.771	−18155.080
$2p_{1/2}$	−17453.400	−17478.696	−17395.916	−17404.377
$2p_{3/2}$	−14710.009	−14724.147	−14670.134	−14678.614
$3s_{1/2}$	−4534.875	−4539.763	−4530.529	−4531.371
$3p_{1/2}$	−4210.285	−4214.905	−4198.867	−4200.484
$3p_{3/2}$	−3581.451	−3584.580	−3574.571	−3576.194
$3d_{3/2}$	−3062.551	−3063.105	−3056.081	−3056.808
$3d_{5/2}$	−2931.328	−2932.272	−2927.465	−2928.167
$4s_{1/2}$	−1123.061	−1124.204	−1122.259	−1122.446
$4p_{1/2}$	−979.253	−980.144	−976.621	−976.989
$4p_{3/2}$	−818.910	−819.626	−817.687	−818.038
$4d_{3/2}$	−586.524	−586.357	−585.377	−585.475
$4d_{5/2}$	−555.989	−556.169	−555.698	−555.791
$4f_{5/2}$	−250.381	−250.182	−250.451	−250.376
$4f_{7/2}$	−243.095	−242.952	−243.445	−243.370
$5s_{1/2}$	−228.619	−228.823	−228.524	−228.547
$5p_{1/2}$	−174.298	−174.398	−173.821	−173.876
$5p_{3/2}$	−140.737	−140.844	−140.601	−140.653
$5d_{3/2}$	−59.683	−59.586	−59.582	−59.577
$5d_{5/2}$	−54.875	−54.875	−54.947	−54.942
$6s_{1/2}$	−29.134	−29.156	−29.138	−29.137
$6p_{1/2}$	−14.703	−14.705	−14.658	−14.661
$6p_{3/2}$	−10.445	−10.450	−10.445	−10.447

Table S32 Orbital fine structure (in eV) of Rn atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	2743.391	2754.549	2725.782	2725.763
$3p_{3/2}-3p_{1/2}$	628.834	630.324	624.296	624.291
$3d_{5/2}-3d_{3/2}$	131.223	130.832	128.616	128.642
$4p_{3/2}-4p_{1/2}$	160.343	160.517	158.934	158.951
$4d_{5/2}-4d_{3/2}$	30.535	30.188	29.679	29.684
$4f_{7/2}-4f_{5/2}$	7.286	7.230	7.006	7.005
$5p_{3/2}-5p_{1/2}$	33.561	33.554	33.220	33.223
$5d_{5/2}-5d_{3/2}$	4.808	4.711	4.635	4.635
$6p_{3/2}-6p_{1/2}$	4.258	4.255	4.214	4.214

Table S33 Orbital energies (in eV) of Og atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−222557.934	−223257.838	−221943.102	−222048.423
$2s$	−46769.018	−46905.562	−46715.209	−46733.897
$2p$	−34398.334	−34423.972	−34215.659	−34245.294
$3s$	−12832.821	−12864.738	−12820.741	−12825.913
$3p$	−9533.576	−9540.773	−9496.093	−9502.587
$3d$	−7465.613	−7468.012	−7446.212	−7449.082
$4s$	−3842.031	−3850.954	−3838.989	−3840.482
$4p$	−2764.858	−2766.678	−2755.530	−2757.223
$4d$	−1982.744	−1983.123	−1979.152	−1979.664
$4f$	−1333.376	−1333.236	−1333.010	−1332.916
$5s$	−1087.630	−1090.181	−1086.986	−1087.379
$5p$	−721.729	−722.135	−719.430	−719.867
$5d$	−429.154	−429.142	−428.638	−428.715
$6s$	−245.032	−245.688	−245.024	−245.096
$6p$	−133.529	−133.579	−133.128	−133.202
$7s$	−34.910	−35.028	−34.966	−34.969
$5f$	−173.124	−172.991	−173.470	−173.390
$6d$	−44.001	−43.964	−44.037	−44.026
$7p$	−10.687	−10.684	−10.661	−10.665

Table S34 Orbital energies (in eV) of Og atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−222183.285	−222770.729	−221449.419	−221533.324
$2s_{1/2}$	−46657.162	−46779.447	−46585.151	−46605.954
$2p_{1/2}$	−45544.782	−45763.583	−45445.816	−45469.365
$2p_{3/2}$	−30928.536	−30981.149	−30821.820	−30847.193
$3s_{1/2}$	−12795.972	−12823.893	−12779.899	−12785.285
$3p_{1/2}$	−12243.474	−12292.593	−12223.847	−12229.623
$3p_{3/2}$	−8649.385	−8662.258	−8628.728	−8634.231
$3d_{3/2}$	−7800.852	−7800.073	−7773.075	−7776.153
$3d_{5/2}$	−7224.549	−7229.346	−7210.222	−7213.134
$4s_{1/2}$	−3829.274	−3836.757	−3824.949	−3826.456
$4p_{1/2}$	−3552.456	−3565.394	−3547.013	−3548.622
$4p_{3/2}$	−2500.583	−2504.069	−2496.202	−2497.584
$4d_{3/2}$	−2076.437	−2075.253	−2069.924	−2070.488
$4d_{5/2}$	−1913.139	−1914.296	−1911.019	−1911.560
$4f_{5/2}$	−1355.939	−1354.881	−1354.016	−1353.960
$4f_{7/2}$	−1307.575	−1307.284	−1307.381	−1307.322
$5s_{1/2}$	−1083.487	−1085.504	−1082.369	−1082.758
$5p_{1/2}$	−953.972	−957.428	−952.538	−952.940
$5p_{3/2}$	−643.027	−643.879	−642.132	−642.481
$5d_{3/2}$	−454.007	−453.412	−452.539	−452.634
$5d_{5/2}$	−409.906	−410.078	−409.734	−409.826
$6s_{1/2}$	−244.124	−244.594	−243.937	−244.008
$6p_{1/2}$	−191.800	−192.583	−191.536	−191.603
$6p_{3/2}$	−114.608	−114.729	−114.498	−114.555
$7s_{1/2}$	−35.235	−35.302	−35.229	−35.233
$5f_{5/2}$	−177.658	−177.169	−177.495	−177.426
$5f_{7/2}$	−167.263	−167.093	−167.622	−167.554
$6d_{3/2}$	−48.200	−47.996	−47.996	−47.991
$6d_{5/2}$	−40.647	−40.621	−40.703	−40.698
$7p_{1/2}$	−20.011	−20.123	−19.998	−20.000
$7p_{3/2}$	−8.318	−8.316	−8.314	−8.317

Table S35 Orbital fine structure (in eV) of Og atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	14616.246	14782.434	14623.997	14622.171
$3p_{3/2}-3p_{1/2}$	3594.090	3630.336	3595.119	3595.393
$3d_{5/2}-3d_{3/2}$	576.302	570.726	562.853	563.019
$4p_{3/2}-4p_{1/2}$	1051.873	1061.324	1050.810	1051.038
$4d_{5/2}-4d_{3/2}$	163.298	160.957	158.905	158.928
$4f_{7/2}-4f_{5/2}$	48.365	47.597	46.636	46.638
$5p_{3/2}-5p_{1/2}$	310.945	313.549	310.405	310.459
$5d_{5/2}-5d_{3/2}$	44.102	43.333	42.805	42.808
$6p_{3/2}-6p_{1/2}$	77.192	77.855	77.038	77.049
$5f_{7/2}-5f_{5/2}$	10.395	10.075	9.873	9.872
$6d_{5/2}-6d_{3/2}$	7.553	7.375	7.293	7.292
$7p_{3/2}-7p_{1/2}$	11.693	11.807	11.684	11.684

S1.3 d-block atoms

Table S36 Orbital energies (in eV) of Zn atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−9729.880	−9734.949	−9722.350	−9723.081
$2s$	−1233.479	−1233.948	−1233.069	−1233.094
$2p$	−1064.935	−1065.153	−1063.821	−1064.000
$3s$	−157.765	−157.828	−157.735	−157.737
$3p$	−105.473	−105.492	−105.360	−105.381
$3d$	−20.717	−20.712	−20.725	−20.723
$4s$	−8.124	−8.126	−8.122	−8.122

Table S37 Orbital energies (in eV) of Zn atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−9729.824	−9734.837	−9722.237	−9722.962
$2s_{1/2}$	−1233.468	−1233.931	−1233.053	−1233.079
$2p_{1/2}$	−1081.134	−1081.387	−1079.706	−1079.884
$2p_{3/2}$	−1056.964	−1057.198	−1056.045	−1056.222
$3s_{1/2}$	−157.764	−157.826	−157.733	−157.736
$3p_{1/2}$	−107.687	−107.698	−107.516	−107.538
$3p_{3/2}$	−104.387	−104.414	−104.308	−104.329
$3d_{3/2}$	−20.978	−20.977	−20.973	−20.971
$3d_{5/2}$	−20.547	−20.537	−20.561	−20.559
$4s_{1/2}$	−8.124	−8.126	−8.123	−8.123

Table S38 Orbital fine structure (in eV) of Zn atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	24.170	24.190	23.662	23.662
$3p_{3/2}-3p_{1/2}$	3.299	3.284	3.209	3.209
$3d_{5/2}-3d_{3/2}$	0.431	0.440	0.412	0.412

Table S39 Orbital energies (in eV) of Cd atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−26846.486	−26868.882	−26809.934	−26814.066
$2s$	−4074.182	−4076.651	−4071.393	−4071.702
$2p$	−3650.560	−3651.806	−3644.047	−3645.129
$3s$	−797.546	−797.972	−797.267	−797.296
$3p$	−654.758	−654.930	−653.854	−654.012
$3d$	−431.120	−431.140	−430.924	−430.942
$4s$	−129.112	−129.180	−129.081	−129.085
$4p$	−84.834	−84.852	−84.713	−84.736
$4d$	−19.613	−19.605	−19.621	−19.619
$5s$	−7.653	−7.657	−7.651	−7.651

Table S40 Orbital energies (in eV) of Cd atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−26845.610	−26867.397	−26808.479	−26812.513
$2s_{1/2}$	−4073.976	−4076.376	−4071.134	−4071.449
$2p_{1/2}$	−3781.375	−3782.998	−3773.461	−3774.518
$2p_{3/2}$	−3588.096	−3589.600	−3582.806	−3583.860
$3s_{1/2}$	−797.486	−797.895	−797.195	−797.224
$3p_{1/2}$	−678.922	−679.060	−677.660	−677.814
$3p_{3/2}$	−643.181	−643.438	−642.538	−642.692
$3d_{3/2}$	−435.364	−435.409	−435.055	−435.074
$3d_{5/2}$	−428.265	−428.260	−428.128	−428.147
$4s_{1/2}$	−129.104	−129.170	−129.071	−129.075
$4p_{1/2}$	−88.997	−89.000	−88.803	−88.826
$4p_{3/2}$	−82.852	−82.887	−82.779	−82.801
$4d_{3/2}$	−20.103	−20.089	−20.088	−20.086
$4d_{5/2}$	−19.294	−19.290	−19.315	−19.314
$5s_{1/2}$	−7.655	−7.658	−7.653	−7.653

Table S41 Orbital fine structure (in eV) of Cd atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	193.278	193.399	190.655	190.658
$3p_{3/2}-3p_{1/2}$	35.741	35.622	35.121	35.122
$3d_{5/2}-3d_{3/2}$	7.099	7.148	6.926	6.927
$4p_{3/2}-4p_{1/2}$	6.145	6.113	6.024	6.025
$4d_{5/2}-4d_{3/2}$	0.809	0.799	0.772	0.772

Table S42 Orbital energies (in eV) of Hg atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−83558.829	−83683.313	−83360.627	−83386.109
$2s$	−14961.606	−14979.283	−14942.571	−14945.578
$2p$	−12957.911	−12965.252	−12915.538	−12922.617
$3s$	−3620.343	−3624.132	−3617.296	−3617.852
$3p$	−3029.399	−3030.887	−3021.642	−3022.981
$3d$	−2377.763	−2378.319	−2374.227	−2374.724
$4s$	−833.665	−834.552	−833.136	−833.260
$4p$	−635.713	−636.002	−634.148	−634.441
$4d$	−390.521	−390.566	−390.108	−390.174
$4f$	−119.391	−119.319	−119.627	−119.572
$5s$	−138.773	−138.925	−138.716	−138.731
$5p$	−82.908	−82.935	−82.698	−82.738
$5d$	−16.441	−16.428	−16.448	−16.446
$6s$	−8.886	−8.898	−8.886	−8.886

Table S43 Orbital energies (in eV) of Hg atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−83539.226	−83654.348	−83332.500	−83356.015
$2s_{1/2}$	−14956.411	−14973.132	−14936.549	−14939.676
$2p_{1/2}$	−14319.296	−14336.426	−14273.570	−14280.172
$2p_{3/2}$	−12374.740	−12385.420	−12343.315	−12349.913
$3s_{1/2}$	−3618.655	−3622.186	−3615.416	−3615.994
$3p_{1/2}$	−3334.198	−3337.155	−3325.219	−3326.451
$3p_{3/2}$	−2896.892	−2899.221	−2891.598	−2892.834
$3d_{3/2}$	−2433.176	−2433.680	−2428.508	−2429.032
$3d_{5/2}$	−2340.060	−2340.707	−2337.210	−2337.717
$4s_{1/2}$	−833.168	−833.977	−832.579	−832.708
$4p_{1/2}$	−710.333	−710.864	−708.319	−708.595
$4p_{3/2}$	−603.251	−603.775	−602.324	−602.589
$4d_{3/2}$	−402.727	−402.633	−401.936	−402.008
$4d_{5/2}$	−382.256	−382.384	−382.055	−382.123
$4f_{5/2}$	−121.820	−121.692	−121.904	−121.850
$4f_{7/2}$	−117.394	−117.305	−117.671	−117.617
$5s_{1/2}$	−138.730	−138.865	−138.657	−138.673
$5p_{1/2}$	−96.232	−96.274	−95.907	−95.944
$5p_{3/2}$	−77.263	−77.337	−77.170	−77.205
$5d_{3/2}$	−17.740	−17.690	−17.685	−17.684
$5d_{5/2}$	−15.632	−15.638	−15.669	−15.667
$6s_{1/2}$	−8.915	−8.925	−8.912	−8.913

Table S44 Orbital fine structure (in eV) of Hg atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	1944.556	1951.006	1930.255	1930.260
$3p_{3/2}-3p_{1/2}$	437.306	437.934	433.621	433.617
$3d_{5/2}-3d_{3/2}$	93.116	92.973	91.297	91.314
$4p_{3/2}-4p_{1/2}$	107.081	107.089	105.995	106.006
$4d_{5/2}-4d_{3/2}$	20.472	20.249	19.881	19.884
$4f_{7/2}-4f_{5/2}$	4.426	4.387	4.233	4.233
$5p_{3/2}-5p_{1/2}$	18.969	18.937	18.737	18.739
$5d_{5/2}-5d_{3/2}$	2.108	2.052	2.016	2.016

Table S45 Orbital energies (in eV) of Cn atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−192212.108	−192735.433	−191662.048	−191748.709
$2s$	−39301.402	−39398.200	−39250.040	−39264.171
$2p$	−30065.292	−30087.165	−29916.300	−29940.636
$3s$	−10637.987	−10660.520	−10627.362	−10631.066
$3p$	−8150.340	−8156.142	−8120.067	−8125.307
$3d$	−6425.567	−6427.621	−6409.933	−6412.249
$4s$	−3089.467	−3095.671	−3086.916	−3087.961
$4p$	−2273.361	−2274.795	−2265.955	−2267.301
$4d$	−1617.453	−1617.778	−1614.638	−1615.048
$4f$	−1039.309	−1039.196	−1039.120	−1039.036
$5s$	−818.583	−820.290	−818.017	−818.287
$5p$	−545.025	−545.335	−543.242	−543.581
$5d$	−304.366	−304.365	−303.965	−304.029
$6s$	−154.237	−154.634	−154.180	−154.229
$5f$	−87.488	−87.396	−87.733	−87.678
$6p$	−76.887	−76.920	−76.591	−76.646
$6d$	−13.260	−13.238	−13.261	−13.258
$7s$	−12.011	−12.060	−12.024	−12.026

Table S46 Orbital energies (in eV) of Cn atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−191978.507	−192425.250	−191350.742	−191422.068
$2s_{1/2}$	−39233.067	−39320.846	−39170.779	−39186.296
$2p_{1/2}$	−38110.424	−38252.192	−38004.919	−38025.098
$2p_{3/2}$	−27362.620	−27404.413	−27270.952	−27292.117
$3s_{1/2}$	−10615.514	−10635.544	−10602.464	−10606.342
$3p_{1/2}$	−10091.091	−10122.289	−10069.724	−10074.345
$3p_{3/2}$	−7472.810	−7482.920	−7455.300	−7459.807
$3d_{3/2}$	−6690.863	−6690.911	−6669.028	−6671.502
$3d_{5/2}$	−6238.481	−6242.271	−6226.749	−6229.099
$4s_{1/2}$	−3081.985	−3087.317	−3078.668	−3079.736
$4p_{1/2}$	−2828.501	−2836.482	−2822.755	−2824.008
$4p_{3/2}$	−2075.599	−2078.325	−2071.936	−2073.051
$4d_{3/2}$	−1690.175	−1689.438	−1685.220	−1685.667
$4d_{5/2}$	−1565.375	−1566.323	−1563.742	−1564.170
$4f_{5/2}$	−1057.292	−1056.606	−1056.028	−1055.968
$4f_{7/2}$	−1021.048	−1020.851	−1021.042	−1020.980
$5s_{1/2}$	−816.543	−817.958	−815.723	−815.993
$5p_{1/2}$	−702.413	−704.439	−700.915	−701.223
$5p_{3/2}$	−489.053	−489.725	−488.326	−488.600
$5d_{3/2}$	−322.892	−322.523	−321.850	−321.923
$5d_{5/2}$	−291.175	−291.349	−291.077	−291.148
$6s_{1/2}$	−154.275	−154.600	−154.151	−154.198
$5f_{5/2}$	−91.042	−90.746	−90.981	−90.931
$5f_{7/2}$	−84.220	−84.149	−84.526	−84.477
$6p_{1/2}$	−111.791	−112.199	−111.514	−111.563
$6p_{3/2}$	−65.621	−65.731	−65.548	−65.589
$7s_{1/2}$	−12.241	−12.279	−12.240	−12.242
$6d_{3/2}$	−15.406	−15.311	−15.304	−15.302
$6d_{5/2}$	−12.019	−12.029	−12.060	−12.058

Table S47 Orbital fine structure (in eV) of Cn atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	10747.804	10847.779	10733.967	10732.981
$3p_{3/2}-3p_{1/2}$	2618.281	2639.369	2614.423	2614.538
$3d_{5/2}-3d_{3/2}$	452.382	448.640	442.279	442.403
$4p_{3/2}-4p_{1/2}$	752.902	758.157	750.820	750.957
$4d_{5/2}-4d_{3/2}$	124.800	123.115	121.478	121.496
$4f_{7/2}-4f_{5/2}$	36.243	35.754	34.986	34.987
$5p_{3/2}-5p_{1/2}$	213.360	214.714	212.589	212.622
$5d_{5/2}-5d_{3/2}$	31.717	31.174	30.773	30.775
$5f_{7/2}-5f_{5/2}$	6.822	6.597	6.455	6.454
$6p_{3/2}-6p_{1/2}$	46.170	46.468	45.966	45.974
$6d_{5/2}-6d_{3/2}$	3.387	3.283	3.244	3.244

S1.4 f-block atoms

Table S48 Orbital energies (in eV) of Yb atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−61641.186	−61718.787	−61513.122	−61528.997
$2s$	−10574.675	−10584.903	−10562.763	−10564.472
$2p$	−9337.461	−9342.167	−9311.338	−9315.712
$3s$	−2439.789	−2441.908	−2437.945	−2438.238
$3p$	−2058.177	−2059.074	−2053.551	−2054.351
$3d$	−1581.127	−1581.450	−1579.158	−1579.428
$4s$	−507.827	−508.304	−507.462	−507.535
$4p$	−379.713	−379.884	−378.782	−378.959
$4d$	−205.816	−205.845	−205.571	−205.614
$5s$	−66.331	−66.394	−66.286	−66.296
$5p$	−34.112	−34.121	−34.021	−34.039
$4f$	−13.802	−13.769	−13.906	−13.885
$6s$	−5.338	−5.341	−5.338	−5.338

Table S49 Orbital energies (in eV) of Yb atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−61632.815	−61705.965	−61500.700	−61515.679
$2s_{1/2}$	−10572.538	−10582.309	−10560.258	−10562.019
$2p_{1/2}$	−10060.945	−10069.715	−10031.434	−10035.591
$2p_{3/2}$	−9013.806	−9020.231	−8993.687	−8997.832
$3s_{1/2}$	−2439.120	−2441.121	−2437.194	−2437.497
$3p_{1/2}$	−2214.257	−2215.611	−2208.582	−2209.333
$3p_{3/2}$	−1987.626	−1988.987	−1984.354	−1985.107
$3d_{3/2}$	−1610.335	−1610.694	−1607.763	−1608.045
$3d_{5/2}$	−1561.361	−1561.677	−1559.748	−1560.023
$4s_{1/2}$	−507.655	−508.103	−507.268	−507.344
$4p_{1/2}$	−415.433	−415.656	−414.187	−414.357
$4p_{3/2}$	−363.617	−363.913	−363.019	−363.184
$4d_{3/2}$	−211.674	−211.649	−211.239	−211.285
$4d_{5/2}$	−201.900	−201.965	−201.764	−201.808
$5s_{1/2}$	−66.324	−66.382	−66.274	−66.284
$5p_{1/2}$	−38.613	−38.617	−38.466	−38.483
$5p_{3/2}$	−32.157	−32.185	−32.110	−32.126
$4f_{5/2}$	−14.723	−14.666	−14.755	−14.734
$4f_{7/2}$	−13.098	−13.066	−13.231	−13.210
$6s_{1/2}$	−5.345	−5.348	−5.344	−5.345

Table S50 Orbital fine structure (in eV) of Yb atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	1047.139	1049.484	1037.747	1037.759
$3p_{3/2}-3p_{1/2}$	226.631	226.623	224.228	224.227
$3d_{5/2}-3d_{3/2}$	48.974	49.016	48.015	48.022
$4p_{3/2}-4p_{1/2}$	51.816	51.743	51.167	51.173
$4d_{5/2}-4d_{3/2}$	9.774	9.684	9.475	9.477
$5p_{3/2}-5p_{1/2}$	6.456	6.432	6.356	6.357
$4f_{7/2}-4f_{5/2}$	1.626	1.600	1.525	1.525

Table S51 Orbital energies (in eV) of No atom with scalar-relativistic Hamiltonians

ε	srX2C	srDC	srDCG	srDCB
$1s$	−150212.793	−150544.033	−149786.408	−149847.770
$2s$	−29445.471	−29501.648	−29403.787	−29412.715
$2p$	−23725.558	−23741.848	−23621.254	−23638.452
$3s$	−7765.156	−7778.035	−7757.246	−7759.373
$3p$	−6193.035	−6197.002	−6172.283	−6175.871
$3d$	−4918.739	−4920.240	−4908.187	−4909.743
$4s$	−2139.817	−2143.249	−2138.031	−2138.608
$4p$	−1619.783	−1620.722	−1614.867	−1615.765
$4d$	−1131.826	−1132.055	−1130.020	−1130.291
$4f$	−661.192	−661.105	−661.200	−661.131
$5s$	−511.848	−512.728	−511.425	−511.571
$5p$	−341.747	−341.938	−340.611	−340.827
$5d$	−169.864	−169.867	−169.611	−169.654
$6s$	−75.865	−76.032	−75.795	−75.821
$6p$	−33.183	−33.195	−33.028	−33.056
$5f$	−14.046	−13.998	−14.161	−14.136
$7s$	−5.629	−5.636	−5.631	−5.631

Table S52 Orbital energies (in eV) of No atom with relativistic Hamiltonians

ε	X2C	DC	DCG	DCB
$1s_{1/2}$	−150103.948	−150394.605	−149638.538	−149691.363
$2s_{1/2}$	−29414.540	−29466.317	−29368.048	−29377.644
$2p_{1/2}$	−28428.577	−28500.372	−28336.296	−28351.306
$2p_{3/2}$	−21980.039	−22008.166	−21911.027	−21926.355
$3s_{1/2}$	−7754.891	−7766.556	−7745.883	−7748.116
$3p_{1/2}$	−7307.724	−7322.727	−7288.844	−7292.027
$3p_{3/2}$	−5767.247	−5773.880	−5754.380	−5757.545
$3d_{3/2}$	−5091.553	−5092.153	−5077.230	−5078.885
$3d_{5/2}$	−4798.861	−4801.265	−4790.706	−4792.286
$4s_{1/2}$	−2136.437	−2139.462	−2134.303	−2134.899
$4p_{1/2}$	−1927.658	−1931.241	−1922.757	−1923.586
$4p_{3/2}$	−1500.625	−1502.363	−1497.965	−1498.734
$4d_{3/2}$	−1176.886	−1176.532	−1173.778	−1174.073
$4d_{5/2}$	−1100.283	−1100.884	−1099.220	−1099.503
$4f_{5/2}$	−672.151	−671.790	−671.553	−671.497
$4f_{7/2}$	−650.892	−650.744	−651.017	−650.962
$5s_{1/2}$	−511.004	−511.762	−510.473	−510.622
$5p_{1/2}$	−422.140	−422.943	−420.894	−421.091
$5p_{3/2}$	−310.820	−311.225	−310.278	−310.461
$5d_{3/2}$	−180.071	−179.880	−179.454	−179.502
$5d_{5/2}$	−162.779	−162.886	−162.706	−162.753
$6s_{1/2}$	−75.928	−76.071	−75.833	−75.858
$6p_{1/2}$	−46.894	−47.013	−46.689	−46.718
$6p_{3/2}$	−28.512	−28.556	−28.451	−28.473
$5f_{5/2}$	−15.566	−15.424	−15.535	−15.512
$5f_{7/2}$	−12.796	−12.770	−12.948	−12.926
$7s_{1/2}$	−5.692	−5.696	−5.689	−5.690

Table S53 Orbital fine structure (in eV) of No atom with relativistic Hamiltonians

$\Delta\varepsilon$	X2C	DC	DCG	DCB
$2p_{3/2}-2p_{1/2}$	6448.538	6492.205	6425.269	6424.951
$3p_{3/2}-3p_{1/2}$	1540.478	1548.847	1534.464	1534.482
$3d_{5/2}-3d_{3/2}$	292.692	290.888	286.525	286.598
$4p_{3/2}-4p_{1/2}$	427.032	428.878	424.792	424.852
$4d_{5/2}-4d_{3/2}$	76.602	75.649	74.559	74.571
$4f_{7/2}-4f_{5/2}$	21.259	21.046	20.536	20.535
$5p_{3/2}-5p_{1/2}$	111.320	111.719	110.615	110.630
$5d_{5/2}-5d_{3/2}$	17.292	16.994	16.748	16.750
$6p_{3/2}-6p_{1/2}$	18.381	18.457	18.238	18.245
$5f_{7/2}-5f_{5/2}$	2.771	2.654	2.587	2.586

S1.5 Basis-set dependence of f-block atoms

In this section, we report effect of changing the basis set on Yb and No orbital energies with srX2C, srDC, X2C, and DC Hamiltonians (see Tables S55 to S66). We investigate Dyall.v2z, Dyall.ae2z, and Dyall.v4z basis sets in addition to reporting the Dyall.ae4z basis set used throughout

this work (see Table S54 for number of basis functions). Note that Dyall.v2z and Dyall.ae2z are the same for Yb atom.

Table S54 Number of basis functions for Yb and No atoms

N^{Bas}	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
Yb	220	220	426	471
No	282	291	495	593

We find no greater than 0.001 eV orbital-energy change when comparing a correlated valence (Dyall.v2z or Dyall.v4z) to a correlated all-shell (Dyall.ae2z or Dyall.ae4z) basis set for both Yb and No atoms. Let us focus on the comparison of Dyall.v2z with Dyall.v4z since the correlated all-shell treatment is not important for occupied orbital energies. For Yb and No, we find no significant changes between an (sr)X2C or a (sr)DC approach in comparing effect of basis set, so let us focus on (sr)X2C results.

For Yb atom with srX2C Hamiltonian, we find about a 0.08 eV difference in $1s$ orbital energy when comparing Dyall.v2z and Dyall.v4z (see Table S55). The orbital-energy difference between the two basis sets is greater than chemical accuracy (0.043 eV) until the $4s$. Orbitals above the $4s$ exhibit energy change less than 0.043 eV.

An X2C Hamiltonian for Yb atom does not obey the same qualitative trend as srX2C (see Table S57). Specifically, we find that the "lower" spinor (e.g., $2p_{1/2}$) is significantly more insensitive to basis set. Below the $4s_{1/2}$ spinor, we find the $2p_{1/2}$ and $2p_{3/2}$ spinors have smaller than chemical accuracy changes when comparing Dyall.v2z with Dyall.v4z. Orbital fine structure is much less sensitive than orbital energies to basis set for Yb atom (see Table S59). The $2p$ fine structure is the only splitting above 0.043 eV.

Table S55 Orbital energies (in eV) of Yb atom with scalar-relativistic X2C Hamiltonians for multiple uncontracted basis sets

	srX2C			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	−61641.255	−61641.255	−61641.186	−61641.186
$2s$	−10574.740	−10574.740	−10574.675	−10574.675
$2p$	−9337.512	−9337.512	−9337.461	−9337.461
$3s$	−2439.840	−2439.840	−2439.789	−2439.789
$3p$	−2058.223	−2058.223	−2058.177	−2058.177
$3d$	−1581.175	−1581.175	−1581.127	−1581.127
$4s$	−507.853	−507.853	−507.827	−507.827
$4p$	−379.736	−379.736	−379.713	−379.713
$4d$	−205.837	−205.837	−205.816	−205.816
$5s$	−66.341	−66.341	−66.331	−66.331
$5p$	−34.116	−34.116	−34.112	−34.112
$4f$	−13.784	−13.784	−13.802	−13.802
$6s$	−5.337	−5.337	−5.338	−5.338

Table S56 Orbital energies (in eV) of Yb atom with scalar-relativistic DC Hamiltonians for multiple uncontracted basis sets

	srDC			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	−61718.855	−61718.855	−61718.787	−61718.787
$2s$	−10584.968	−10584.968	−10584.903	−10584.903
$2p$	−9342.218	−9342.218	−9342.167	−9342.167
$3s$	−2441.960	−2441.960	−2441.908	−2441.908
$3p$	−2059.120	−2059.120	−2059.074	−2059.074
$3d$	−1581.498	−1581.498	−1581.450	−1581.450
$4s$	−508.331	−508.331	−508.304	−508.304
$4p$	−379.907	−379.907	−379.884	−379.884
$4d$	−205.867	−205.867	−205.845	−205.845
$5s$	−66.405	−66.405	−66.394	−66.394
$5p$	−34.126	−34.126	−34.121	−34.121
$4f$	−13.751	−13.751	−13.769	−13.769
$6s$	−5.340	−5.340	−5.341	−5.341

Table S57 Orbital energies (in eV) of Yb atom with X2C Hamiltonian for multiple uncontracted basis sets

	X2C			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	−61632.889	−61632.889	−61632.815	−61632.815
$2s_{1/2}$	−10572.602	−10572.602	−10572.538	−10572.538
$2p_{1/2}$	−10060.926	−10060.926	−10060.945	−10060.945
$2p_{3/2}$	−9013.864	−9013.864	−9013.806	−9013.806
$3s_{1/2}$	−2439.170	−2439.170	−2439.120	−2439.120
$3p_{1/2}$	−2214.284	−2214.284	−2214.257	−2214.257
$3p_{3/2}$	−1987.672	−1987.672	−1987.626	−1987.626
$3d_{3/2}$	−1610.378	−1610.378	−1610.335	−1610.335
$3d_{5/2}$	−1561.409	−1561.409	−1561.361	−1561.361
$4s_{1/2}$	−507.679	−507.679	−507.655	−507.655
$4p_{1/2}$	−415.451	−415.451	−415.433	−415.433
$4p_{3/2}$	−363.638	−363.638	−363.617	−363.617
$4d_{3/2}$	−211.692	−211.692	−211.674	−211.674
$4d_{5/2}$	−201.920	−201.920	−201.900	−201.900
$5s_{1/2}$	−66.333	−66.333	−66.324	−66.324
$5p_{1/2}$	−38.612	−38.612	−38.613	−38.613
$5p_{3/2}$	−32.161	−32.161	−32.157	−32.157
$4f_{5/2}$	−14.701	−14.701	−14.723	−14.723
$4f_{7/2}$	−13.078	−13.078	−13.098	−13.098
$6s_{1/2}$	−5.344	−5.344	−5.345	−5.345

Table S58 Orbital energies (in eV) of Yb atom with DC Hamiltonian for multiple uncontracted basis sets

	DC			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	−61706.042	−61706.042	−61705.965	−61705.965
$2s_{1/2}$	−10582.375	−10582.375	−10582.309	−10582.309
$2p_{1/2}$	−10069.693	−10069.693	−10069.715	−10069.715
$2p_{3/2}$	−9020.290	−9020.290	−9020.231	−9020.231
$3s_{1/2}$	−2441.172	−2441.172	−2441.121	−2441.121
$3p_{1/2}$	−2215.638	−2215.638	−2215.611	−2215.611
$3p_{3/2}$	−1989.034	−1989.034	−1988.988	−1988.987
$3d_{3/2}$	−1610.737	−1610.737	−1610.694	−1610.694
$3d_{5/2}$	−1561.726	−1561.726	−1561.677	−1561.677
$4s_{1/2}$	−508.128	−508.128	−508.103	−508.103
$4p_{1/2}$	−415.674	−415.674	−415.656	−415.656
$4p_{3/2}$	−363.935	−363.935	−363.913	−363.913
$4d_{3/2}$	−211.667	−211.667	−211.649	−211.649
$4d_{5/2}$	−201.985	−201.985	−201.965	−201.965
$5s_{1/2}$	−66.391	−66.391	−66.382	−66.382
$5p_{1/2}$	−38.617	−38.617	−38.617	−38.617
$5p_{3/2}$	−32.189	−32.189	−32.185	−32.185
$4f_{5/2}$	−14.643	−14.643	−14.666	−14.666
$4f_{7/2}$	−13.048	−13.048	−13.066	−13.066
$6s_{1/2}$	−5.346	−5.346	−5.348	−5.348

Table S59 Orbital fine structure (in eV) of Yb atom with X2C Hamiltonian for multiple uncontracted basis sets

	X2C			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$2p_{3/2}-2p_{1/2}$	1047.063	1047.063	1047.139	1047.139
$3p_{3/2}-3p_{1/2}$	226.613	226.613	226.631	226.631
$3d_{5/2}-3d_{3/2}$	48.969	48.969	48.974	48.974
$4p_{3/2}-4p_{1/2}$	51.812	51.812	51.816	51.816
$4d_{5/2}-4d_{3/2}$	9.773	9.773	9.774	9.774
$5p_{3/2}-5p_{1/2}$	6.451	6.451	6.456	6.456
$4f_{7/2}-4f_{5/2}$	1.622	1.622	1.626	1.626

Table S60 Orbital fine structure (in eV) of Yb atom with DC Hamiltonian for multiple uncontracted basis sets

	DC			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$2p_{3/2}-2p_{1/2}$	1049.403	1049.403	1049.484	1049.484
$3p_{3/2}-3p_{1/2}$	226.604	226.604	226.623	226.623
$3d_{5/2}-3d_{3/2}$	49.011	49.011	49.016	49.016
$4p_{3/2}-4p_{1/2}$	51.739	51.739	51.743	51.743
$4d_{5/2}-4d_{3/2}$	9.683	9.683	9.684	9.684
$5p_{3/2}-5p_{1/2}$	6.427	6.427	6.432	6.432
$4f_{7/2}-4f_{5/2}$	1.595	1.595	1.600	1.600

Unlike Yb atom, No atom exhibits no change (between Dyall.v2z and Dyall.v4z) of orbital energy with a srX2C Hamiltonian larger than 0.043 eV (see Table S61).

When comparing Dyall.v2z and Dyall.v4z, an X2C Hamiltonian for No atom behaves differently from both Yb atom and No atom with srX2C Hamiltonian (see Table S63). The $2p_{1/2}$ exhibits a drastic change (0.072 eV), while even $1s_{1/2}$ exhibits a change less than 0.043 eV. The orbital fine structure of No atom follows the same trend as the X2C orbital energies (see Table S65).

Table S61 Orbital energies (in eV) of No atom with scalar-relativistic X2C Hamiltonians for multiple uncontracted basis sets

	srX2C			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	−150212.817	−150212.817	−150212.794	−150212.793
$2s$	−29445.490	−29445.490	−29445.471	−29445.471
$2p$	−23725.566	−23725.566	−23725.558	−23725.558
$3s$	−7765.167	−7765.167	−7765.156	−7765.156
$3p$	−6193.041	−6193.041	−6193.035	−6193.035
$3d$	−4918.749	−4918.749	−4918.739	−4918.739
$4s$	−2139.819	−2139.819	−2139.817	−2139.817
$4p$	−1619.783	−1619.783	−1619.783	−1619.783
$4d$	−1131.828	−1131.828	−1131.826	−1131.826
$4f$	−661.180	−661.180	−661.192	−661.192
$5s$	−511.847	−511.847	−511.848	−511.848
$5p$	−341.743	−341.743	−341.747	−341.747
$5d$	−169.862	−169.862	−169.864	−169.864
$6s$	−75.865	−75.865	−75.865	−75.865
$6p$	−33.178	−33.178	−33.183	−33.183
$5f$	−14.034	−14.034	−14.046	−14.046
$7s$	−5.630	−5.630	−5.629	−5.629

Table S62 Orbital energies (in eV) of No atom with scalar-relativistic DC Hamiltonians for multiple uncontracted basis sets

	srDC			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	−150544.056	−150544.056	−150544.033	−150544.033
$2s$	−29501.667	−29501.667	−29501.648	−29501.648
$2p$	−23741.856	−23741.856	−23741.848	−23741.848
$3s$	−7778.047	−7778.047	−7778.036	−7778.035
$3p$	−6197.008	−6197.008	−6197.002	−6197.002
$3d$	−4920.250	−4920.250	−4920.240	−4920.240
$4s$	−2143.252	−2143.252	−2143.249	−2143.249
$4p$	−1620.722	−1620.722	−1620.722	−1620.722
$4d$	−1132.057	−1132.057	−1132.055	−1132.055
$4f$	−661.093	−661.093	−661.104	−661.105
$5s$	−512.727	−512.727	−512.728	−512.728
$5p$	−341.934	−341.934	−341.938	−341.938
$5d$	−169.867	−169.867	−169.867	−169.867
$6s$	−76.032	−76.032	−76.032	−76.032
$6p$	−33.190	−33.190	−33.195	−33.195
$5f$	−13.987	−13.987	−13.998	−13.998
$7s$	−5.637	−5.637	−5.636	−5.636

Table S63 Orbital energies (in eV) of No atom with X2C Hamiltonian for multiple uncontracted basis sets

	X2C			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	−150103.973	−150103.973	−150103.948	−150103.948
$2s_{1/2}$	−29414.555	−29414.555	−29414.540	−29414.540
$2p_{1/2}$	−28428.505	−28428.505	−28428.577	−28428.577
$2p_{3/2}$	−21980.047	−21980.047	−21980.039	−21980.039
$3s_{1/2}$	−7754.896	−7754.896	−7754.891	−7754.891
$3p_{1/2}$	−7307.704	−7307.704	−7307.725	−7307.724
$3p_{3/2}$	−5767.247	−5767.247	−5767.247	−5767.247
$3d_{3/2}$	−5091.554	−5091.554	−5091.553	−5091.553
$3d_{5/2}$	−4798.866	−4798.866	−4798.861	−4798.861
$4s_{1/2}$	−2136.433	−2136.433	−2136.437	−2136.437
$4p_{1/2}$	−1927.643	−1927.643	−1927.658	−1927.658
$4p_{3/2}$	−1500.619	−1500.619	−1500.626	−1500.625
$4d_{3/2}$	−1176.881	−1176.881	−1176.886	−1176.886
$4d_{5/2}$	−1100.279	−1100.279	−1100.283	−1100.283
$4f_{5/2}$	−672.128	−672.128	−672.150	−672.151
$4f_{7/2}$	−650.875	−650.875	−650.892	−650.892
$5s_{1/2}$	−510.997	−510.997	−511.004	−511.004
$5p_{1/2}$	−422.126	−422.126	−422.140	−422.140
$5p_{3/2}$	−310.811	−310.811	−310.820	−310.820
$5d_{3/2}$	−180.062	−180.062	−180.071	−180.071
$5d_{5/2}$	−162.771	−162.771	−162.779	−162.779
$6s_{1/2}$	−75.923	−75.923	−75.928	−75.928
$6p_{1/2}$	−46.875	−46.875	−46.894	−46.894
$6p_{3/2}$	−28.504	−28.504	−28.512	−28.512
$5f_{5/2}$	−15.547	−15.547	−15.566	−15.566
$5f_{7/2}$	−12.777	−12.777	−12.796	−12.796
$7s_{1/2}$	−5.692	−5.692	−5.692	−5.692

Table S64 Orbital energies (in eV) of No atom with DC Hamiltonian for multiple uncontracted basis sets

	DC			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	−150394.634	−150394.634	−150394.606	−150394.605
$2s_{1/2}$	−29466.334	−29466.334	−29466.317	−29466.317
$2p_{1/2}$	−28500.297	−28500.297	−28500.372	−28500.372
$2p_{3/2}$	−22008.175	−22008.175	−22008.166	−22008.166
$3s_{1/2}$	−7766.562	−7766.562	−7766.556	−7766.556
$3p_{1/2}$	−7322.706	−7322.706	−7322.727	−7322.727
$3p_{3/2}$	−5773.882	−5773.882	−5773.880	−5773.880
$3d_{3/2}$	−5092.154	−5092.154	−5092.153	−5092.153
$3d_{5/2}$	−4801.271	−4801.271	−4801.265	−4801.265
$4s_{1/2}$	−2139.459	−2139.459	−2139.462	−2139.462
$4p_{1/2}$	−1931.227	−1931.227	−1931.241	−1931.241
$4p_{3/2}$	−1502.357	−1502.357	−1502.363	−1502.363
$4d_{3/2}$	−1176.528	−1176.528	−1176.532	−1176.532
$4d_{5/2}$	−1100.880	−1100.880	−1100.884	−1100.884
$4f_{5/2}$	−671.767	−671.767	−671.790	−671.790
$4f_{7/2}$	−650.729	−650.729	−650.744	−650.744
$5s_{1/2}$	−511.755	−511.755	−511.762	−511.762
$5p_{1/2}$	−422.929	−422.929	−422.943	−422.943
$5p_{3/2}$	−311.215	−311.215	−311.225	−311.225
$5d_{3/2}$	−179.872	−179.872	−179.880	−179.880
$5d_{5/2}$	−162.879	−162.879	−162.886	−162.886
$6s_{1/2}$	−76.066	−76.066	−76.071	−76.071
$6p_{1/2}$	−46.994	−46.994	−47.013	−47.013
$6p_{3/2}$	−28.548	−28.548	−28.556	−28.556
$5f_{5/2}$	−15.405	−15.405	−15.424	−15.424
$5f_{7/2}$	−12.753	−12.753	−12.770	−12.770
$7s_{1/2}$	−5.696	−5.696	−5.696	−5.696

Table S65 Orbital fine structure (in eV) of No atom with X2C Hamiltonian for multiple uncontracted basis sets

	X2C			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$2p_{3/2}-2p_{1/2}$	6448.459	6448.459	6448.538	6448.538
$3p_{3/2}-3p_{1/2}$	1540.456	1540.456	1540.478	1540.478
$3d_{5/2}-3d_{3/2}$	292.689	292.689	292.692	292.692
$4p_{3/2}-4p_{1/2}$	427.024	427.024	427.032	427.032
$4d_{5/2}-4d_{3/2}$	76.601	76.601	76.602	76.602
$4f_{7/2}-4f_{5/2}$	21.253	21.253	21.259	21.259
$5p_{3/2}-5p_{1/2}$	111.315	111.315	111.320	111.320
$5d_{5/2}-5d_{3/2}$	17.291	17.291	17.292	17.292
$6p_{3/2}-6p_{1/2}$	18.371	18.371	18.381	18.381
$5f_{7/2}-5f_{5/2}$	2.769	2.769	2.771	2.771

Table S66 Orbital fine structure (in eV) of No atom with DC Hamiltonian for multiple uncontracted basis sets

	DC			
ε	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$2p_{3/2}-2p_{1/2}$	6492.121	6492.121	6492.205	6492.205
$3p_{3/2}-3p_{1/2}$	1548.825	1548.825	1548.847	1548.847
$3d_{5/2}-3d_{3/2}$	290.884	290.884	290.888	290.888
$4p_{3/2}-4p_{1/2}$	428.870	428.870	428.878	428.878
$4d_{5/2}-4d_{3/2}$	75.648	75.648	75.649	75.649
$4f_{7/2}-4f_{5/2}$	21.038	21.038	21.045	21.046
$5p_{3/2}-5p_{1/2}$	111.714	111.714	111.719	111.719
$5d_{5/2}-5d_{3/2}$	16.993	16.993	16.994	16.994
$6p_{3/2}-6p_{1/2}$	18.446	18.446	18.457	18.457
$5f_{7/2}-5f_{5/2}$	2.653	2.653	2.654	2.654

S2 Radial property computational details

For the radial orbital properties, the radial part of the orbital is needed. We calculated the radial component by integrating the angular part of the wave function with a Lebedev angular grid containing 974 points. We explicitly included the formal 4π prefactor (i.e., angular integration of a constant C equals $4\pi C$).

The radial grid was logarithmic, determined by a starting radial point r_0, a final radial point r_f, and number of points N_p. A point in the radial loop over counter i is determined by

$$r_i = r_0 \left(\exp\left(\frac{\log r_f - \log r_0}{N_p - 1} \right) \right)^i . \tag{S1}$$

Radial expectation values are calculated numerically via the trapezoidal rule over the above grid by

$$\langle r \rangle \approx \frac{\sum_{i=1}^{N_p-1} \left(r_i P_i + r_{i-1} P_{i-1} \right) \Delta r_i}{\sum_{i=1}^{N_p-1} \left(P_i + P_{i-1} \right) \Delta r_i} \quad \text{with} \quad \Delta r_i = r_i - r_{i-1} \tag{S2}$$

where

$$P = P(r) = 4\pi r^2 \left| \psi^{\text{rad}}(r) \right|^2 \tag{S3}$$

and ψ^{rad} is the radial wave function. This work used the following grid parameters: $r_0 = 1 \times 10^{-6}$ a.u., $r_f = 10.0$ a.u., and $N_p = 500$. All two-component radial properties in this work have picture-change error, and all four-component radial properties were calculated with the large-component contribution only. See next section for more details on the latter approximation.

S3 Radial wave function approximations

For both radial expectation value and radial distribution functions discussed in the previous section, we approximate the radial wave function as the large component of the radial wave function in four-component calculations. This approximation is good for the majority of the data in this manuscript, but we show below cases where the approximation should be relaxed in future work.

By analyzing the radial normalization (denominator of Equation (S2)), we can investigate both quality of radial grid and radial wave function. Since the 4-component radial wave function neglects small component, comparison of radial normalization tests the quality of the large-component radial approximation. We report radial normalization for selected p-block atoms in Table S67. We show scalar Hamiltonians because the qualitative findings are unchanged when adding vector relativity. For atoms tested, all orbitals not shown have $> 99\%$ radial normalization.

Table S67 Radial normalization of selected atoms and orbitals for scalar Hamiltonians.

	$\sum_{i=1}^{N_p-1}\left(P_i+P_{i-1}\right)\Delta r_i$	srX2C	srDC	srDCG	srDCB
Kr	$1s$	1.00	0.98	0.98	0.98
Xe	$1s$	1.00	0.96	0.96	0.96
Rn	$1s$	1.00	0.89	0.89	0.89
	$2s$	1.00	0.97	0.97	0.97
	$2p$	1.00	0.98	0.98	0.98
Og	$1s$	1.00	0.76	0.76	0.76
	$2s$	1.00	0.94	0.94	0.94
	$2p$	1.00	0.95	0.95	0.95
	$3s$	1.00	0.98	0.98	0.98
	$3p$	1.00	0.98	0.98	0.98
	$3d$	1.00	0.98	0.98	0.98

As we see in Table S67, the radial grid is sufficiently converged as indicated by unity in the srX2C column. For four-component Hamiltonians we see no change in the contribution of the small component to radial normalization. Since no change is observed for srDC → srDCB Hamiltonian substitution, we expect no significant change to relative radial quantities when comparing between (sr)DC, (sr)DCG, and (sr)DCB Hamiltonians upon relaxing the large-component approximation.

S4 Radial expectation values

In this section we report radial expectation values for all atoms investigated in this work. The one-electron exact 2-component (X2C), Dirac–Coulomb (DC), Dirac–Coulomb–Gaunt (DCG), and Dirac–Coulomb-Breit (DCB) Hamiltonians are explored along with their scalar-relativistic counterparts (denoted with a preceding "sr"). Focus should be placed on relative shift and not on absolute value since (sr)X2C has picture-change error of Coulomb operator and the 4-component Hamiltonians do not include small-component contributions, which can be sizable for core orbitals of heavy elements (see preceding section).

S4.1 s-block atoms

Table S68 Orbital radial expectation values (in a.u.) of Be atom with scalar-relativistic Hamiltonians

$\langle r\rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.415	0.415	0.415	0.415
$2s$	2.648	2.648	2.648	2.648

Table S69 Orbital radial expectation values (in a.u.) of Be atom with relativistic Hamiltonians

$\langle r\rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.415	0.415	0.415	0.415
$2s_{1/2}$	2.648	2.648	2.648	2.648

Table S70 Orbital radial expectation values (in a.u.) of Mg atom with scalar-relativistic Hamiltonians

$\langle r\rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.130	0.130	0.130	0.130
$2s$	0.689	0.689	0.689	0.689
$2p$	0.685	0.685	0.685	0.685
$3s$	3.244	3.244	3.244	3.244

Table S71 Orbital radial expectation values (in a.u.) of Mg atom with relativistic Hamiltonians

$\langle r\rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.130	0.130	0.130	0.130
$2s_{1/2}$	0.689	0.689	0.689	0.689
$2p_{1/2}$	0.683	0.683	0.684	0.684
$2p_{3/2}$	0.685	0.685	0.686	0.686
$3s_{1/2}$	3.244	3.244	3.244	3.244

Table S72 Orbital radial expectation values (in a.u.) of Ca atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.077	0.077	0.077	0.077
$2s$	0.361	0.361	0.361	0.361
$2p$	0.326	0.326	0.326	0.326
$3s$	1.154	1.154	1.154	1.154
$3p$	1.273	1.273	1.274	1.274
$4s$	4.175	4.174	4.175	4.175

Table S73 Orbital radial expectation values (in a.u.) of Ca atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.077	0.077	0.077	0.077
$2s_{1/2}$	0.361	0.361	0.361	0.361
$2p_{1/2}$	0.325	0.325	0.325	0.325
$2p_{3/2}$	0.327	0.327	0.327	0.327
$3s_{1/2}$	1.154	1.154	1.154	1.154
$3p_{1/2}$	1.268	1.268	1.269	1.269
$3p_{3/2}$	1.276	1.276	1.276	1.276
$4s_{1/2}$	4.175	4.174	4.175	4.175

Table S74 Orbital radial expectation values (in a.u.) of Sr atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.039	0.039	0.039	0.039
$2s$	0.172	0.172	0.172	0.172
$2p$	0.150	0.150	0.151	0.151
$3s$	0.489	0.489	0.489	0.489
$3p$	0.496	0.496	0.496	0.496
$3d$	0.496	0.497	0.497	0.497
$4s$	1.366	1.366	1.367	1.367
$4p$	1.570	1.570	1.571	1.571
$5s$	4.517	4.516	4.517	4.517

Table S75 Orbital radial expectation values (in a.u.) of Sr atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.039	0.039	0.039	0.039
$2s_{1/2}$	0.172	0.172	0.172	0.172
$2p_{1/2}$	0.148	0.148	0.148	0.148
$2p_{3/2}$	0.151	0.152	0.152	0.152
$3s_{1/2}$	0.489	0.489	0.489	0.489
$3p_{1/2}$	0.489	0.489	0.490	0.490
$3p_{3/2}$	0.499	0.499	0.500	0.499
$3d_{3/2}$	0.495	0.495	0.495	0.495
$3d_{5/2}$	0.498	0.498	0.498	0.498
$4s_{1/2}$	1.366	1.366	1.367	1.367
$4p_{1/2}$	1.549	1.549	1.550	1.550
$4p_{3/2}$	1.581	1.581	1.581	1.581
$5s_{1/2}$	4.517	4.516	4.517	4.517

Table S76 Orbital radial expectation values (in a.u.) of Ba atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.025	0.026	0.026	0.026
$2s$	0.109	0.110	0.110	0.110
$2p$	0.096	0.096	0.096	0.096
$3s$	0.290	0.291	0.291	0.291
$3p$	0.288	0.289	0.289	0.289
$3d$	0.266	0.266	0.266	0.266
$4s$	0.674	0.674	0.674	0.674
$4p$	0.715	0.715	0.716	0.715
$4d$	0.801	0.801	0.801	0.801
$5s$	1.657	1.657	1.658	1.658
$5p$	1.924	1.924	1.926	1.925
$6s$	4.991	4.990	4.991	4.991

Table S77 Orbital radial expectation values (in a.u.) of Ba atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.025	0.026	0.026	0.026
$2s_{1/2}$	0.109	0.110	0.110	0.110
$2p_{1/2}$	0.092	0.093	0.093	0.093
$2p_{3/2}$	0.098	0.098	0.098	0.098
$3s_{1/2}$	0.290	0.291	0.291	0.291
$3p_{1/2}$	0.281	0.281	0.282	0.282
$3p_{3/2}$	0.292	0.293	0.293	0.293
$3d_{3/2}$	0.264	0.264	0.264	0.264
$3d_{5/2}$	0.267	0.267	0.267	0.267
$4s_{1/2}$	0.674	0.674	0.674	0.674
$4p_{1/2}$	0.698	0.698	0.699	0.699
$4p_{3/2}$	0.723	0.723	0.724	0.724
$4d_{3/2}$	0.795	0.795	0.796	0.796
$4d_{5/2}$	0.805	0.805	0.805	0.805
$5s_{1/2}$	1.657	1.657	1.658	1.658
$5p_{1/2}$	1.871	1.871	1.873	1.872
$5p_{3/2}$	1.951	1.951	1.952	1.952
$6s_{1/2}$	4.990	4.989	4.990	4.990

Table S78 Orbital radial expectation values (in a.u.) of Ra atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.014	0.015	0.015	0.015
$2s$	0.060	0.061	0.061	0.061
$2p$	0.056	0.056	0.056	0.056
$3s$	0.157	0.158	0.158	0.158
$3p$	0.160	0.161	0.161	0.161
$3d$	0.146	0.147	0.147	0.147
$4s$	0.343	0.344	0.345	0.344
$4p$	0.366	0.367	0.368	0.367
$4d$	0.383	0.384	0.384	0.384
$4f$	0.387	0.387	0.387	0.387
$5s$	0.738	0.738	0.738	0.738
$5p$	0.826	0.826	0.827	0.827
$5d$	0.996	0.996	0.997	0.997
$6s$	1.706	1.705	1.707	1.707
$6p$	2.090	2.090	2.093	2.092
$7s$	4.959	4.957	4.958	4.958

Table S79 Orbital radial expectation values (in a.u.) of Ra atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.014	0.015	0.015	0.015
$2s_{1/2}$	0.060	0.061	0.061	0.061
$2p_{1/2}$	0.050	0.050	0.050	0.050
$2p_{3/2}$	0.058	0.059	0.059	0.059
$3s_{1/2}$	0.157	0.158	0.158	0.158
$3p_{1/2}$	0.148	0.149	0.149	0.149
$3p_{3/2}$	0.165	0.166	0.166	0.166
$3d_{3/2}$	0.144	0.144	0.144	0.144
$3d_{5/2}$	0.148	0.149	0.149	0.149
$4s_{1/2}$	0.344	0.344	0.345	0.345
$4p_{1/2}$	0.343	0.344	0.345	0.344
$4p_{3/2}$	0.377	0.378	0.378	0.378
$4d_{3/2}$	0.377	0.377	0.378	0.378
$4d_{5/2}$	0.387	0.388	0.388	0.388
$4f_{5/2}$	0.384	0.385	0.385	0.385
$4f_{7/2}$	0.389	0.390	0.390	0.390
$5s_{1/2}$	0.738	0.738	0.739	0.738
$5p_{1/2}$	0.774	0.774	0.775	0.775
$5p_{3/2}$	0.850	0.851	0.852	0.851
$5d_{3/2}$	0.979	0.979	0.980	0.980
$5d_{5/2}$	1.009	1.010	1.010	1.010
$6s_{1/2}$	1.705	1.705	1.706	1.706
$6p_{1/2}$	1.925	1.924	1.927	1.927
$6p_{3/2}$	2.173	2.172	2.174	2.174
$7s_{1/2}$	4.948	4.947	4.948	4.948

S4.2 p-block atoms

Table S80 Orbital radial expectation values (in a.u.) of Ne atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.157	0.157	0.157	0.157
$2s$	0.891	0.891	0.891	0.891
$2p$	0.965	0.965	0.965	0.965

Table S81 Orbital radial expectation values (in a.u.) of Ne atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.157	0.157	0.157	0.157
$2s_{1/2}$	0.891	0.891	0.891	0.891
$2p_{1/2}$	0.963	0.963	0.964	0.964
$2p_{3/2}$	0.966	0.966	0.966	0.966

Table S82 Orbital radial expectation values (in a.u.) of Ar atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.085	0.086	0.086	0.086
$2s$	0.410	0.410	0.410	0.410
$2p$	0.375	0.375	0.375	0.375
$3s$	1.416	1.416	1.416	1.416
$3p$	1.662	1.662	1.663	1.663

Table S83 Orbital radial expectation values (in a.u.) of Ar atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.085	0.086	0.086	0.086
$2s_{1/2}$	0.410	0.410	0.410	0.410
$2p_{1/2}$	0.373	0.373	0.373	0.373
$2p_{3/2}$	0.375	0.375	0.376	0.375
$3s_{1/2}$	1.416	1.416	1.416	1.416
$3p_{1/2}$	1.656	1.656	1.656	1.656
$3p_{3/2}$	1.665	1.665	1.666	1.666

Table S84 Orbital radial expectation values (in a.u.) of Kr atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.041	0.041	0.042	0.042
$2s$	0.183	0.183	0.183	0.183
$2p$	0.160	0.160	0.160	0.160
$3s$	0.527	0.527	0.528	0.528
$3p$	0.538	0.538	0.539	0.539
$3d$	0.553	0.553	0.553	0.553
$4s$	1.601	1.601	1.601	1.601
$4p$	1.944	1.944	1.945	1.945

Table S85 Orbital radial expectation values (in a.u.) of Kr atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.041	0.041	0.042	0.042
$2s_{1/2}$	0.183	0.183	0.183	0.183
$2p_{1/2}$	0.158	0.158	0.158	0.158
$2p_{3/2}$	0.161	0.161	0.161	0.161
$3s_{1/2}$	0.527	0.527	0.528	0.528
$3p_{1/2}$	0.532	0.532	0.532	0.532
$3p_{3/2}$	0.541	0.541	0.542	0.542
$3d_{3/2}$	0.551	0.551	0.551	0.551
$3d_{5/2}$	0.554	0.554	0.554	0.554
$4s_{1/2}$	1.601	1.601	1.601	1.601
$4p_{1/2}$	1.915	1.915	1.916	1.916
$4p_{3/2}$	1.959	1.959	1.959	1.959

Table S86 Orbital radial expectation values (in a.u.) of Xe atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.026	0.027	0.027	0.027
$2s$	0.114	0.115	0.115	0.115
$2p$	0.100	0.100	0.101	0.100
$3s$	0.305	0.305	0.305	0.305
$3p$	0.303	0.303	0.304	0.304
$3d$	0.280	0.280	0.280	0.280
$4s$	0.717	0.718	0.718	0.718
$4p$	0.765	0.765	0.766	0.765
$4d$	0.876	0.876	0.877	0.877
$5s$	1.905	1.905	1.906	1.906
$5p$	2.315	2.315	2.316	2.316

Table S87 Orbital radial expectation values (in a.u.) of Xe atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.026	0.027	0.027	0.027
$2s_{1/2}$	0.114	0.115	0.115	0.115
$2p_{1/2}$	0.097	0.097	0.097	0.097
$2p_{3/2}$	0.102	0.102	0.102	0.102
$3s_{1/2}$	0.305	0.305	0.305	0.305
$3p_{1/2}$	0.295	0.296	0.296	0.296
$3p_{3/2}$	0.307	0.307	0.307	0.307
$3d_{3/2}$	0.278	0.278	0.278	0.278
$3d_{5/2}$	0.281	0.281	0.282	0.282
$4s_{1/2}$	0.717	0.718	0.718	0.718
$4p_{1/2}$	0.747	0.748	0.749	0.748
$4p_{3/2}$	0.773	0.773	0.774	0.774
$4d_{3/2}$	0.870	0.870	0.871	0.871
$4d_{5/2}$	0.880	0.881	0.881	0.881
$5s_{1/2}$	1.905	1.905	1.906	1.906
$5p_{1/2}$	2.241	2.241	2.244	2.243
$5p_{3/2}$	2.352	2.352	2.353	2.353

Table S88 Orbital radial expectation values (in a.u.) of Rn atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.014	0.015	0.015	0.015
$2s$	0.062	0.063	0.063	0.063
$2p$	0.057	0.058	0.058	0.058
$3s$	0.162	0.163	0.163	0.163
$3p$	0.165	0.165	0.166	0.166
$3d$	0.151	0.151	0.151	0.151
$4s$	0.356	0.357	0.357	0.357
$4p$	0.379	0.380	0.381	0.380
$4d$	0.398	0.398	0.398	0.398
$4f$	0.406	0.407	0.407	0.407
$5s$	0.776	0.776	0.777	0.777
$5p$	0.872	0.872	0.873	0.873
$5d$	1.075	1.076	1.076	1.076
$6s$	1.923	1.922	1.924	1.924
$6p$	2.467	2.467	2.470	2.469

Table S89 Orbital radial expectation values (in a.u.) of Rn atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.014	0.015	0.015	0.015
$2s_{1/2}$	0.062	0.063	0.063	0.063
$2p_{1/2}$	0.052	0.052	0.052	0.052
$2p_{3/2}$	0.060	0.061	0.061	0.061
$3s_{1/2}$	0.162	0.163	0.163	0.163
$3p_{1/2}$	0.154	0.154	0.155	0.154
$3p_{3/2}$	0.170	0.171	0.171	0.171
$3d_{3/2}$	0.148	0.148	0.148	0.148
$3d_{5/2}$	0.152	0.153	0.153	0.153
$4s_{1/2}$	0.356	0.357	0.357	0.357
$4p_{1/2}$	0.357	0.357	0.358	0.358
$4p_{3/2}$	0.390	0.391	0.391	0.391
$4d_{3/2}$	0.391	0.392	0.392	0.392
$4d_{5/2}$	0.402	0.402	0.403	0.403
$4f_{5/2}$	0.404	0.404	0.404	0.404
$4f_{7/2}$	0.409	0.409	0.409	0.409
$5s_{1/2}$	0.776	0.776	0.777	0.777
$5p_{1/2}$	0.818	0.819	0.820	0.820
$5p_{3/2}$	0.898	0.898	0.899	0.899
$5d_{3/2}$	1.056	1.057	1.057	1.057
$5d_{5/2}$	1.090	1.090	1.091	1.090
$6s_{1/2}$	1.922	1.921	1.922	1.922
$6p_{1/2}$	2.242	2.242	2.246	2.246
$6p_{3/2}$	2.583	2.582	2.585	2.584

Table S90 Orbital radial expectation values (in a.u.) of Og atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.008	0.009	0.009	0.009
$2s$	0.036	0.037	0.037	0.037
$2p$	0.037	0.038	0.038	0.038
$3s$	0.097	0.098	0.098	0.098
$3p$	0.107	0.108	0.108	0.108
$3d$	0.101	0.102	0.102	0.102
$4s$	0.208	0.209	0.209	0.209
$4p$	0.235	0.236	0.237	0.237
$4d$	0.246	0.247	0.247	0.247
$4f$	0.233	0.233	0.233	0.233
$5s$	0.410	0.410	0.411	0.411
$5p$	0.474	0.475	0.476	0.476
$5d$	0.536	0.537	0.537	0.537
$6s$	0.813	0.813	0.814	0.814
$5f$	0.613	0.613	0.613	0.613
$6p$	0.996	0.996	0.998	0.998
$6d$	1.302	1.303	1.303	1.303
$7s$	1.849	1.846	1.849	1.849
$7p$	2.650	2.650	2.655	2.654

Table S91 Orbital radial expectation values (in a.u.) of Og atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.008	0.009	0.009	0.009
$2s_{1/2}$	0.036	0.037	0.037	0.037
$2p_{1/2}$	0.028	0.029	0.029	0.029
$2p_{3/2}$	0.041	0.042	0.042	0.042
$3s_{1/2}$	0.097	0.098	0.098	0.098
$3p_{1/2}$	0.089	0.090	0.090	0.090
$3p_{3/2}$	0.114	0.115	0.116	0.116
$3d_{3/2}$	0.098	0.098	0.099	0.099
$3d_{5/2}$	0.104	0.104	0.105	0.105
$4s_{1/2}$	0.208	0.209	0.210	0.209
$4p_{1/2}$	0.203	0.204	0.205	0.205
$4p_{3/2}$	0.249	0.249	0.250	0.250
$4d_{3/2}$	0.240	0.240	0.241	0.241
$4d_{5/2}$	0.251	0.252	0.252	0.252
$4f_{5/2}$	0.230	0.231	0.231	0.231
$4f_{7/2}$	0.235	0.236	0.236	0.236
$5s_{1/2}$	0.410	0.411	0.412	0.411
$5p_{1/2}$	0.415	0.415	0.416	0.416
$5p_{3/2}$	0.500	0.501	0.501	0.501
$5d_{3/2}$	0.523	0.523	0.524	0.524
$5d_{5/2}$	0.547	0.547	0.548	0.548
$6s_{1/2}$	0.813	0.813	0.814	0.814
$6p_{1/2}$	0.853	0.852	0.855	0.855
$5f_{5/2}$	0.607	0.607	0.607	0.607
$5f_{7/2}$	0.620	0.621	0.621	0.621
$6p_{3/2}$	1.061	1.060	1.062	1.062
$6d_{3/2}$	1.264	1.266	1.267	1.266
$6d_{5/2}$	1.341	1.341	1.342	1.342
$7s_{1/2}$	1.839	1.837	1.840	1.839
$7p_{1/2}$	2.079	2.073	2.080	2.080
$7p_{3/2}$	2.967	2.967	2.969	2.968

S4.3 d-block atoms

Table S92 Orbital radial expectation values (in a.u.) of Zn atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.050	0.050	0.050	0.050
$2s$	0.225	0.225	0.225	0.225
$2p$	0.198	0.198	0.198	0.198
$3s$	0.681	0.681	0.681	0.681
$3p$	0.715	0.715	0.716	0.716
$3d$	0.880	0.880	0.880	0.880
$4s$	2.848	2.847	2.849	2.848

Table S93 Orbital radial expectation values (in a.u.) of Zn atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.050	0.050	0.050	0.050
$2s_{1/2}$	0.225	0.225	0.225	0.225
$2p_{1/2}$	0.196	0.196	0.196	0.196
$2p_{3/2}$	0.199	0.199	0.199	0.199
$3s_{1/2}$	0.681	0.681	0.681	0.681
$3p_{1/2}$	0.709	0.709	0.709	0.709
$3p_{3/2}$	0.719	0.719	0.719	0.719
$3d_{3/2}$	0.876	0.876	0.876	0.876
$3d_{5/2}$	0.883	0.883	0.883	0.883
$4s_{1/2}$	2.848	2.847	2.848	2.848

Table S94 Orbital radial expectation values (in a.u.) of Cd atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.030	0.030	0.030	0.030
$2s$	0.131	0.131	0.132	0.132
$2p$	0.115	0.115	0.115	0.115
$3s$	0.356	0.356	0.357	0.357
$3p$	0.355	0.356	0.356	0.356
$3d$	0.334	0.334	0.334	0.334
$4s$	0.885	0.885	0.886	0.886
$4p$	0.967	0.967	0.968	0.968
$4d$	1.266	1.266	1.266	1.266
$5s$	3.089	3.087	3.089	3.089

Table S95 Orbital radial expectation values (in a.u.) of Cd atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.030	0.030	0.030	0.030
$2s_{1/2}$	0.131	0.131	0.132	0.132
$2p_{1/2}$	0.112	0.112	0.112	0.112
$2p_{3/2}$	0.116	0.116	0.117	0.117
$3s_{1/2}$	0.356	0.357	0.357	0.357
$3p_{1/2}$	0.348	0.349	0.349	0.349
$3p_{3/2}$	0.359	0.359	0.359	0.359
$3d_{3/2}$	0.332	0.332	0.332	0.332
$3d_{5/2}$	0.335	0.335	0.335	0.335
$4s_{1/2}$	0.885	0.886	0.886	0.886
$4p_{1/2}$	0.948	0.948	0.949	0.949
$4p_{3/2}$	0.977	0.977	0.978	0.978
$4d_{3/2}$	1.254	1.254	1.255	1.255
$4d_{5/2}$	1.274	1.274	1.274	1.274
$5s_{1/2}$	3.088	3.087	3.089	3.089

Table S96 Orbital radial expectation values (in a.u.) of Hg atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.016	0.017	0.017	0.017
$2s$	0.069	0.070	0.070	0.070
$2p$	0.063	0.063	0.063	0.063
$3s$	0.180	0.181	0.181	0.181
$3p$	0.181	0.182	0.182	0.182
$3d$	0.165	0.165	0.166	0.166
$4s$	0.399	0.400	0.400	0.400
$4p$	0.424	0.424	0.425	0.425
$4d$	0.448	0.448	0.449	0.449
$5s$	0.916	0.916	0.917	0.916
$4f$	0.480	0.480	0.480	0.480
$5p$	1.049	1.049	1.051	1.051
$5d$	1.470	1.471	1.471	1.471
$6s$	2.849	2.847	2.850	2.850

Table S97 Orbital radial expectation values (in a.u.) of Hg atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.016	0.017	0.017	0.017
$2s_{1/2}$	0.069	0.070	0.070	0.070
$2p_{1/2}$	0.057	0.058	0.058	0.058
$2p_{3/2}$	0.065	0.066	0.066	0.066
$3s_{1/2}$	0.180	0.181	0.181	0.181
$3p_{1/2}$	0.171	0.171	0.172	0.172
$3p_{3/2}$	0.186	0.187	0.187	0.187
$3d_{3/2}$	0.163	0.163	0.163	0.163
$3d_{5/2}$	0.167	0.167	0.167	0.167
$4s_{1/2}$	0.399	0.400	0.400	0.400
$4p_{1/2}$	0.402	0.402	0.403	0.403
$4p_{3/2}$	0.434	0.434	0.435	0.435
$4d_{3/2}$	0.442	0.442	0.443	0.443
$4d_{5/2}$	0.452	0.453	0.453	0.453
$5s_{1/2}$	0.916	0.916	0.917	0.916
$4f_{5/2}$	0.477	0.477	0.477	0.477
$4f_{7/2}$	0.483	0.483	0.483	0.483
$5p_{1/2}$	0.988	0.988	0.989	0.989
$5p_{3/2}$	1.080	1.079	1.081	1.081
$5d_{3/2}$	1.430	1.431	1.432	1.432
$5d_{5/2}$	1.499	1.499	1.499	1.499
$6s_{1/2}$	2.845	2.843	2.846	2.846

Table S98 Orbital radial expectation values (in a.u.) of Cn atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.009	0.010	0.010	0.010
$2s$	0.040	0.041	0.041	0.041
$2p$	0.040	0.041	0.041	0.041
$3s$	0.107	0.108	0.108	0.108
$3p$	0.115	0.116	0.117	0.117
$3d$	0.108	0.109	0.109	0.109
$4s$	0.229	0.230	0.230	0.230
$4p$	0.255	0.255	0.256	0.256
$4d$	0.266	0.266	0.267	0.266
$4f$	0.252	0.253	0.253	0.253
$5s$	0.457	0.457	0.458	0.458
$5p$	0.522	0.523	0.524	0.524
$5d$	0.594	0.594	0.595	0.595
$6s$	0.943	0.943	0.944	0.944
$5f$	0.710	0.711	0.711	0.711
$6p$	1.169	1.169	1.172	1.171
$6d$	1.728	1.728	1.729	1.729
$7s$	2.517	2.512	2.517	2.516

Table S99 Orbital radial expectation values (in a.u.) of Cn atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.009	0.010	0.010	0.010
$2s_{1/2}$	0.040	0.041	0.041	0.041
$2p_{1/2}$	0.032	0.032	0.033	0.032
$2p_{3/2}$	0.044	0.045	0.045	0.045
$3s_{1/2}$	0.107	0.108	0.108	0.108
$3p_{1/2}$	0.099	0.100	0.100	0.100
$3p_{3/2}$	0.122	0.123	0.123	0.123
$3d_{3/2}$	0.105	0.105	0.106	0.105
$3d_{5/2}$	0.111	0.111	0.111	0.111
$4s_{1/2}$	0.229	0.230	0.231	0.231
$4p_{1/2}$	0.225	0.226	0.227	0.227
$4p_{3/2}$	0.267	0.268	0.269	0.269
$4d_{3/2}$	0.259	0.260	0.260	0.260
$4d_{5/2}$	0.270	0.271	0.271	0.271
$4f_{5/2}$	0.250	0.250	0.251	0.250
$4f_{7/2}$	0.255	0.255	0.255	0.255
$5s_{1/2}$	0.457	0.457	0.458	0.458
$5p_{1/2}$	0.465	0.465	0.467	0.467
$5p_{3/2}$	0.547	0.548	0.549	0.549
$5d_{3/2}$	0.580	0.580	0.581	0.581
$5d_{5/2}$	0.605	0.605	0.606	0.606
$6s_{1/2}$	0.943	0.942	0.944	0.943
$5f_{5/2}$	0.703	0.703	0.703	0.703
$5f_{7/2}$	0.719	0.719	0.719	0.719
$6p_{1/2}$	1.009	1.008	1.011	1.010
$6p_{3/2}$	1.245	1.244	1.246	1.246
$7s_{1/2}$	2.502	2.499	2.503	2.503
$6d_{3/2}$	1.641	1.643	1.645	1.645
$6d_{5/2}$	1.796	1.795	1.795	1.795

S4.4 f-block atoms

Table S100 Orbital radial expectation values (in a.u.) of Yb atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.019	0.020	0.020	0.020
$2s$	0.083	0.083	0.083	0.083
$2p$	0.074	0.074	0.074	0.074
$3s$	0.216	0.216	0.217	0.217
$3p$	0.215	0.216	0.216	0.216
$3d$	0.196	0.196	0.196	0.196
$4s$	0.489	0.489	0.490	0.489
$4p$	0.518	0.518	0.519	0.519
$4d$	0.562	0.563	0.563	0.563
$5s$	1.235	1.235	1.236	1.236
$5p$	1.468	1.468	1.471	1.470
$4f$	0.754	0.754	0.753	0.753
$6s$	4.209	4.207	4.209	4.209

Table S101 Orbital radial expectation values (in a.u.) of Yb atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.019	0.020	0.020	0.020
$2s_{1/2}$	0.083	0.083	0.083	0.083
$2p_{1/2}$	0.069	0.069	0.070	0.070
$2p_{3/2}$	0.076	0.076	0.076	0.076
$3s_{1/2}$	0.216	0.216	0.217	0.217
$3p_{1/2}$	0.206	0.207	0.207	0.207
$3p_{3/2}$	0.220	0.220	0.220	0.220
$3d_{3/2}$	0.194	0.194	0.194	0.194
$3d_{5/2}$	0.198	0.198	0.198	0.198
$4s_{1/2}$	0.489	0.489	0.490	0.490
$4p_{1/2}$	0.498	0.498	0.499	0.499
$4p_{3/2}$	0.528	0.528	0.529	0.529
$4d_{3/2}$	0.556	0.556	0.557	0.557
$4d_{5/2}$	0.567	0.567	0.568	0.568
$5s_{1/2}$	1.235	1.234	1.236	1.236
$5p_{1/2}$	1.391	1.391	1.394	1.393
$5p_{3/2}$	1.507	1.507	1.509	1.508
$4f_{5/2}$	0.744	0.744	0.744	0.744
$4f_{7/2}$	0.762	0.762	0.761	0.761
$6s_{1/2}$	4.205	4.203	4.206	4.206

Table S102 Orbital radial expectation values (in a.u.) of No atom with scalar-relativistic Hamiltonians

$\langle r \rangle$	srX2C	srDC	srDCG	srDCB
$1s$	0.011	0.012	0.012	0.012
$2s$	0.048	0.049	0.049	0.049
$2p$	0.046	0.046	0.047	0.047
$3s$	0.125	0.126	0.126	0.126
$3p$	0.131	0.132	0.132	0.132
$3d$	0.122	0.122	0.122	0.122
$4s$	0.270	0.271	0.271	0.271
$4p$	0.293	0.294	0.295	0.294
$4d$	0.305	0.305	0.306	0.306
$4f$	0.294	0.294	0.295	0.294
$5s$	0.551	0.551	0.552	0.552
$5p$	0.621	0.622	0.623	0.623
$5d$	0.722	0.722	0.723	0.723
$6s$	1.230	1.229	1.231	1.230
$6p$	1.557	1.557	1.561	1.560
$5f$	1.036	1.036	1.035	1.035
$7s$	4.042	4.037	4.041	4.041

Table S103 Orbital radial expectation values (in a.u.) of No atom with relativistic Hamiltonians

$\langle r \rangle$	X2C	DC	DCG	DCB
$1s_{1/2}$	0.011	0.012	0.012	0.012
$2s_{1/2}$	0.048	0.049	0.049	0.049
$2p_{1/2}$	0.039	0.039	0.039	0.039
$2p_{3/2}$	0.049	0.050	0.050	0.050
$3s_{1/2}$	0.125	0.126	0.127	0.126
$3p_{1/2}$	0.117	0.118	0.118	0.118
$3p_{3/2}$	0.138	0.138	0.139	0.139
$3d_{3/2}$	0.119	0.119	0.119	0.119
$3d_{5/2}$	0.124	0.124	0.124	0.124
$4s_{1/2}$	0.270	0.271	0.271	0.271
$4p_{1/2}$	0.267	0.268	0.268	0.268
$4p_{3/2}$	0.305	0.306	0.306	0.306
$4d_{3/2}$	0.299	0.299	0.300	0.300
$4d_{5/2}$	0.309	0.310	0.310	0.310
$4f_{5/2}$	0.292	0.292	0.292	0.292
$4f_{7/2}$	0.296	0.297	0.297	0.297
$5s_{1/2}$	0.551	0.551	0.552	0.552
$5p_{1/2}$	0.567	0.567	0.569	0.568
$5p_{3/2}$	0.646	0.646	0.648	0.647
$5d_{3/2}$	0.706	0.706	0.707	0.707
$5d_{5/2}$	0.734	0.734	0.735	0.735
$6s_{1/2}$	1.228	1.227	1.229	1.229
$6p_{1/2}$	1.357	1.355	1.360	1.359
$6p_{3/2}$	1.658	1.656	1.660	1.659
$5f_{5/2}$	1.014	1.015	1.015	1.015
$5f_{7/2}$	1.057	1.058	1.056	1.056
$7s_{1/2}$	4.015	4.012	4.016	4.016

S4.5 Basis-set dependence of f-block atoms

In this section, we report effect of changing the basis set on Yb and No radial expectation values with srX2C, srDC, X2C, and DC Hamiltonians (see Tables S104 to S111). We investigate Dyall.v2z, Dyall.ae2z, and Dyall.v4z basis sets in addition to reporting the Dyall.ae4z basis set used throughout this work (see Table S54 for number of basis functions). We find little to no change in radial expectation value as a function of basis set. Note that these results do not include the small component.

Table S104 Orbital radial expectation values (in a.u.) of Yb atom with scalar-relativistic X2C Hamiltonian using several uncontracted basis sets

	srX2C			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	0.019	0.019	0.019	0.019
$2s$	0.083	0.083	0.083	0.083
$2p$	0.074	0.074	0.074	0.074
$3s$	0.216	0.216	0.216	0.216
$3p$	0.215	0.215	0.215	0.215
$3d$	0.196	0.196	0.196	0.196
$4s$	0.489	0.489	0.489	0.489
$4p$	0.518	0.518	0.518	0.518
$4d$	0.562	0.562	0.562	0.562
$5s$	1.235	1.235	1.235	1.235
$5p$	1.468	1.468	1.468	1.468
$4f$	0.754	0.754	0.754	0.754
$6s$	4.210	4.210	4.209	4.209

Table S105 Orbital radial expectation values (in a.u.) of Yb atom with scalar-relativistic DC Hamiltonian using several uncontracted basis sets

	srDC			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	0.020	0.020	0.020	0.020
$2s$	0.083	0.083	0.083	0.083
$2p$	0.074	0.074	0.074	0.074
$3s$	0.216	0.216	0.216	0.216
$3p$	0.216	0.216	0.216	0.216
$3d$	0.196	0.196	0.196	0.196
$4s$	0.489	0.489	0.489	0.489
$4p$	0.518	0.518	0.518	0.518
$4d$	0.563	0.563	0.563	0.563
$5s$	1.235	1.235	1.235	1.235
$5p$	1.467	1.467	1.468	1.468
$4f$	0.754	0.754	0.754	0.754
$6s$	4.208	4.208	4.207	4.207

Table S106 Orbital radial expectation values (in a.u.) of Yb atom with relativistic X2C Hamiltonian using several uncontracted basis sets

	X2C			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	0.019	0.019	0.019	0.019
$2s_{1/2}$	0.083	0.083	0.083	0.083
$2p_{1/2}$	0.069	0.069	0.069	0.069
$2p_{3/2}$	0.076	0.076	0.076	0.076
$3s_{1/2}$	0.216	0.216	0.216	0.216
$3p_{1/2}$	0.206	0.206	0.206	0.206
$3p_{3/2}$	0.220	0.220	0.220	0.220
$3d_{3/2}$	0.194	0.194	0.194	0.194
$3d_{5/2}$	0.198	0.198	0.198	0.198
$4s_{1/2}$	0.489	0.489	0.489	0.489
$4p_{1/2}$	0.498	0.498	0.498	0.498
$4p_{3/2}$	0.528	0.528	0.528	0.528
$4d_{3/2}$	0.556	0.556	0.556	0.556
$4d_{5/2}$	0.567	0.567	0.567	0.567
$5s_{1/2}$	1.235	1.235	1.235	1.235
$5p_{1/2}$	1.391	1.391	1.391	1.391
$5p_{3/2}$	1.506	1.506	1.507	1.507
$4f_{5/2}$	0.744	0.744	0.744	0.744
$4f_{7/2}$	0.762	0.762	0.762	0.762
$6s_{1/2}$	4.206	4.206	4.205	4.205

Table S107 Orbital radial expectation values (in a.u.) of Yb atom with relativistic DC Hamiltonian using several uncontracted basis sets

	DC			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	0.020	0.020	0.020	0.020
$2s_{1/2}$	0.083	0.083	0.083	0.083
$2p_{1/2}$	0.069	0.069	0.069	0.069
$2p_{3/2}$	0.076	0.076	0.076	0.076
$3s_{1/2}$	0.216	0.216	0.216	0.216
$3p_{1/2}$	0.207	0.207	0.207	0.207
$3p_{3/2}$	0.220	0.220	0.220	0.220
$3d_{3/2}$	0.194	0.194	0.194	0.194
$3d_{5/2}$	0.198	0.198	0.198	0.198
$4s_{1/2}$	0.489	0.489	0.489	0.489
$4p_{1/2}$	0.498	0.498	0.498	0.498
$4p_{3/2}$	0.528	0.528	0.528	0.528
$4d_{3/2}$	0.556	0.556	0.556	0.556
$4d_{5/2}$	0.567	0.567	0.567	0.567
$5s_{1/2}$	1.234	1.234	1.234	1.234
$5p_{1/2}$	1.391	1.391	1.391	1.391
$5p_{3/2}$	1.505	1.505	1.507	1.507
$4f_{5/2}$	0.745	0.745	0.744	0.744
$4f_{7/2}$	0.763	0.763	0.762	0.762
$6s_{1/2}$	4.205	4.205	4.203	4.203

Table S108 Orbital radial expectation values (in a.u.) of No atom with scalar-relativistic X2C Hamiltonian using several uncontracted basis sets

	srX2C			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	0.011	0.011	0.011	0.011
$2s$	0.048	0.048	0.048	0.048
$2p$	0.046	0.046	0.046	0.046
$3s$	0.125	0.125	0.125	0.125
$3p$	0.131	0.131	0.131	0.131
$3d$	0.122	0.122	0.122	0.122
$4s$	0.270	0.270	0.270	0.270
$4p$	0.293	0.293	0.293	0.293
$4d$	0.305	0.305	0.305	0.305
$4f$	0.294	0.294	0.294	0.294
$5s$	0.551	0.551	0.551	0.551
$5p$	0.621	0.621	0.621	0.621
$5d$	0.722	0.722	0.722	0.722
$6s$	1.230	1.230	1.230	1.230
$6p$	1.557	1.557	1.557	1.557
$5f$	1.036	1.036	1.036	1.036
$7s$	4.043	4.043	4.042	4.042

Table S109 Orbital radial expectation values (in a.u.) of No atom with scalar-relativistic DC Hamiltonian using several uncontracted basis sets

	srDC			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s$	0.012	0.012	0.012	0.012
$2s$	0.049	0.049	0.049	0.049
$2p$	0.046	0.046	0.046	0.046
$3s$	0.126	0.126	0.126	0.126
$3p$	0.132	0.132	0.132	0.132
$3d$	0.122	0.122	0.122	0.122
$4s$	0.271	0.271	0.271	0.271
$4p$	0.294	0.294	0.294	0.294
$4d$	0.305	0.305	0.305	0.305
$4f$	0.294	0.294	0.294	0.294
$5s$	0.551	0.551	0.551	0.551
$5p$	0.622	0.622	0.622	0.622
$5d$	0.722	0.722	0.722	0.722
$6s$	1.229	1.229	1.229	1.229
$6p$	1.557	1.557	1.557	1.557
$5f$	1.037	1.037	1.036	1.036
$7s$	4.039	4.039	4.037	4.037

Table S110 Orbital radial expectation values (in a.u.) of No atom with relativistic X2C Hamiltonian using several uncontracted basis sets

	X2C			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	0.011	0.011	0.011	0.011
$2s_{1/2}$	0.048	0.048	0.048	0.048
$2p_{1/2}$	0.039	0.039	0.039	0.039
$2p_{3/2}$	0.049	0.049	0.049	0.049
$3s_{1/2}$	0.125	0.125	0.125	0.125
$3p_{1/2}$	0.117	0.117	0.117	0.117
$3p_{3/2}$	0.138	0.138	0.138	0.138
$3d_{3/2}$	0.119	0.119	0.119	0.119
$3d_{5/2}$	0.124	0.124	0.124	0.124
$4s_{1/2}$	0.270	0.270	0.270	0.270
$4p_{1/2}$	0.267	0.267	0.267	0.267
$4p_{3/2}$	0.305	0.305	0.305	0.305
$4d_{3/2}$	0.299	0.299	0.299	0.299
$4d_{5/2}$	0.309	0.309	0.309	0.309
$4f_{5/2}$	0.292	0.292	0.292	0.292
$4f_{7/2}$	0.296	0.296	0.296	0.296
$5s_{1/2}$	0.551	0.551	0.551	0.551
$5p_{1/2}$	0.567	0.567	0.567	0.567
$5p_{3/2}$	0.646	0.646	0.646	0.646
$5d_{3/2}$	0.706	0.706	0.706	0.706
$5d_{5/2}$	0.734	0.734	0.734	0.734
$6s_{1/2}$	1.228	1.228	1.228	1.228
$6p_{1/2}$	1.357	1.357	1.357	1.357
$6p_{3/2}$	1.657	1.657	1.658	1.658
$5f_{5/2}$	1.014	1.014	1.014	1.014
$5f_{7/2}$	1.058	1.058	1.057	1.057
$7s_{1/2}$	4.017	4.017	4.015	4.015

Table S111 Orbital radial expectation values (in a.u.) of No atom with relativistic DC Hamiltonian using several uncontracted basis sets

	DC			
$\langle r \rangle$	Dyall.v2z	Dyall.ae2z	Dyall.v4z	Dyall.ae4z
$1s_{1/2}$	0.012	0.012	0.012	0.012
$2s_{1/2}$	0.049	0.049	0.049	0.049
$2p_{1/2}$	0.039	0.039	0.039	0.039
$2p_{3/2}$	0.050	0.050	0.050	0.050
$3s_{1/2}$	0.126	0.126	0.126	0.126
$3p_{1/2}$	0.118	0.118	0.118	0.118
$3p_{3/2}$	0.138	0.138	0.138	0.138
$3d_{3/2}$	0.119	0.119	0.119	0.119
$3d_{5/2}$	0.124	0.124	0.124	0.124
$4s_{1/2}$	0.271	0.271	0.271	0.271
$4p_{1/2}$	0.268	0.268	0.268	0.268
$4p_{3/2}$	0.306	0.306	0.306	0.306
$4d_{3/2}$	0.299	0.299	0.299	0.299
$4d_{5/2}$	0.310	0.310	0.310	0.310
$4f_{5/2}$	0.292	0.292	0.292	0.292
$4f_{7/2}$	0.297	0.297	0.297	0.297
$5s_{1/2}$	0.551	0.551	0.551	0.551
$5p_{1/2}$	0.567	0.567	0.567	0.567
$5p_{3/2}$	0.646	0.646	0.646	0.646
$5d_{3/2}$	0.706	0.706	0.706	0.706
$5d_{5/2}$	0.734	0.734	0.734	0.734
$6s_{1/2}$	1.227	1.227	1.227	1.227
$6p_{1/2}$	1.356	1.356	1.355	1.355
$6p_{3/2}$	1.655	1.655	1.656	1.656
$5f_{5/2}$	1.016	1.016	1.015	1.015
$5f_{7/2}$	1.058	1.058	1.058	1.058
$7s_{1/2}$	4.014	4.014	4.012	4.012

S5 Radial distribution functions

In this section we report radial distribution functions for all atoms investigated in this work. We compare scalar-relativistic Dirac–Coulomb (srDC) with DC to characterize the effect of spin–own–orbit coupling. As discussed in the previous two sections, both Hamiltonians do not include small-component contributions, which can be sizable for core orbitals of heavy elements.

S5.1 s-block atoms

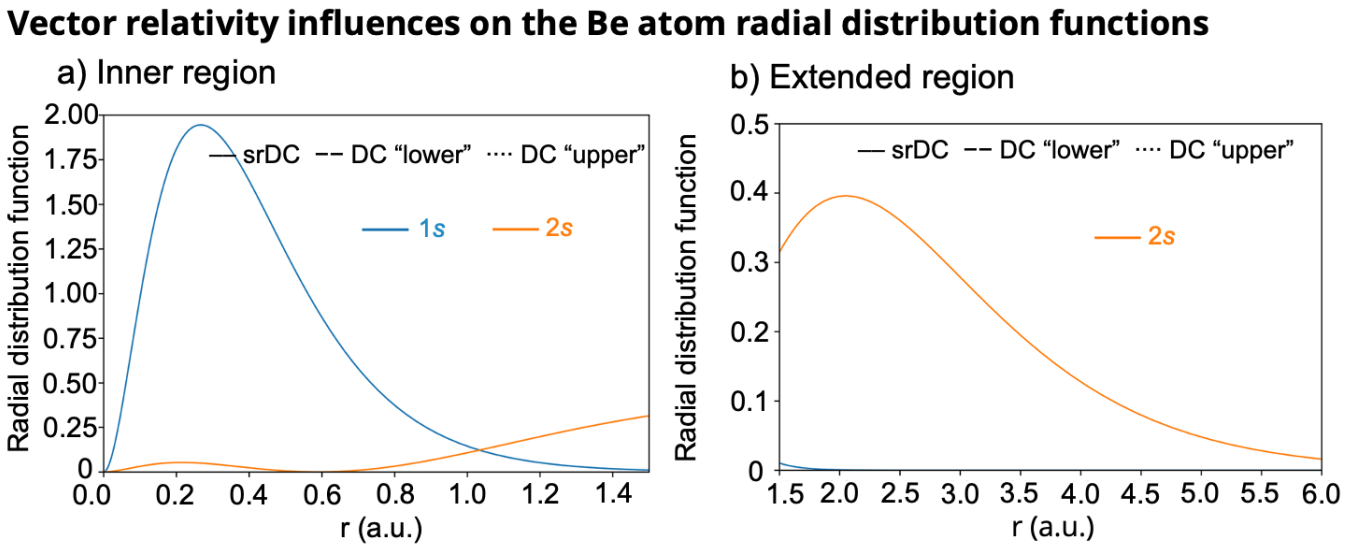

Figure S1 Orbital radial distribution functions for Be atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

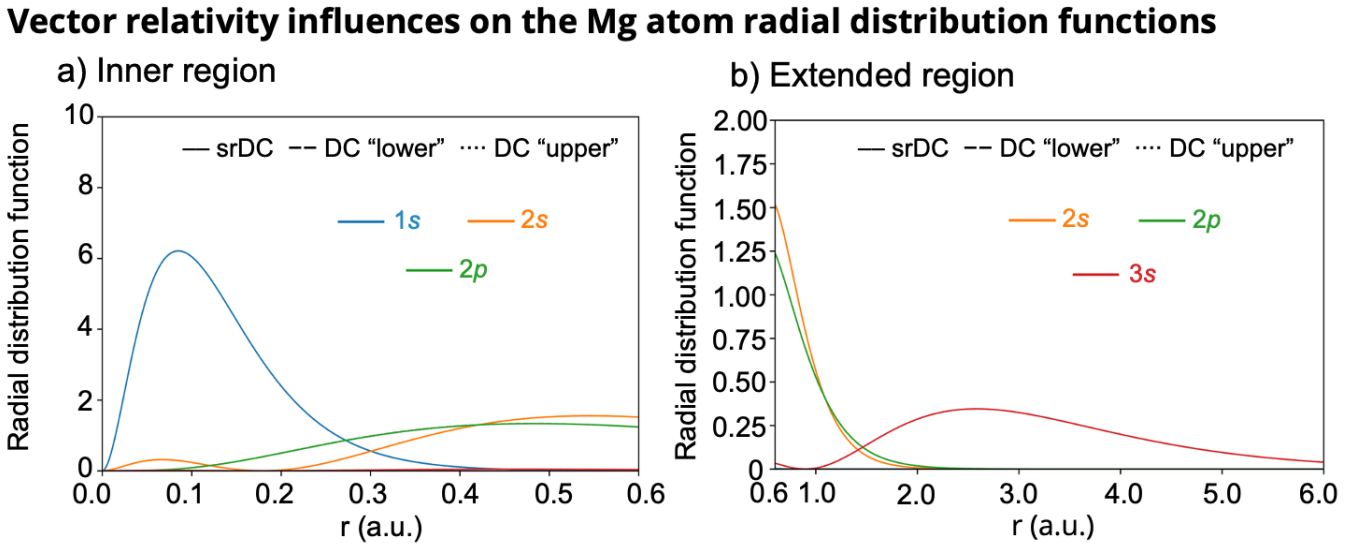

Figure S2 Orbital radial distribution functions for Mg atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

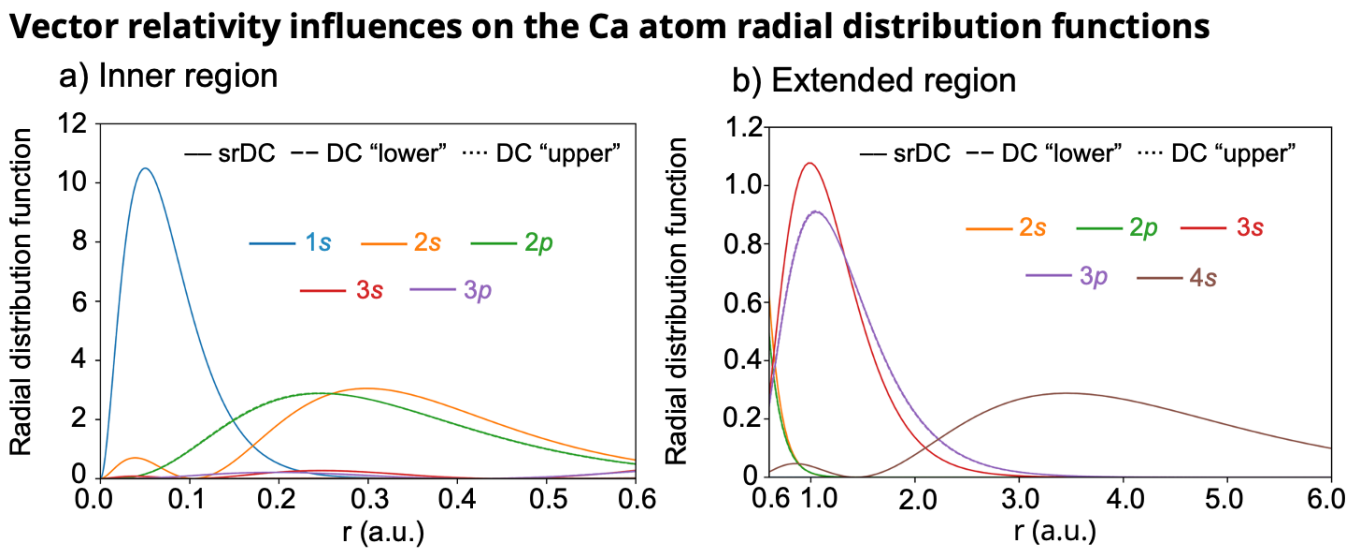

Figure S3 Orbital radial distribution functions for Ca atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

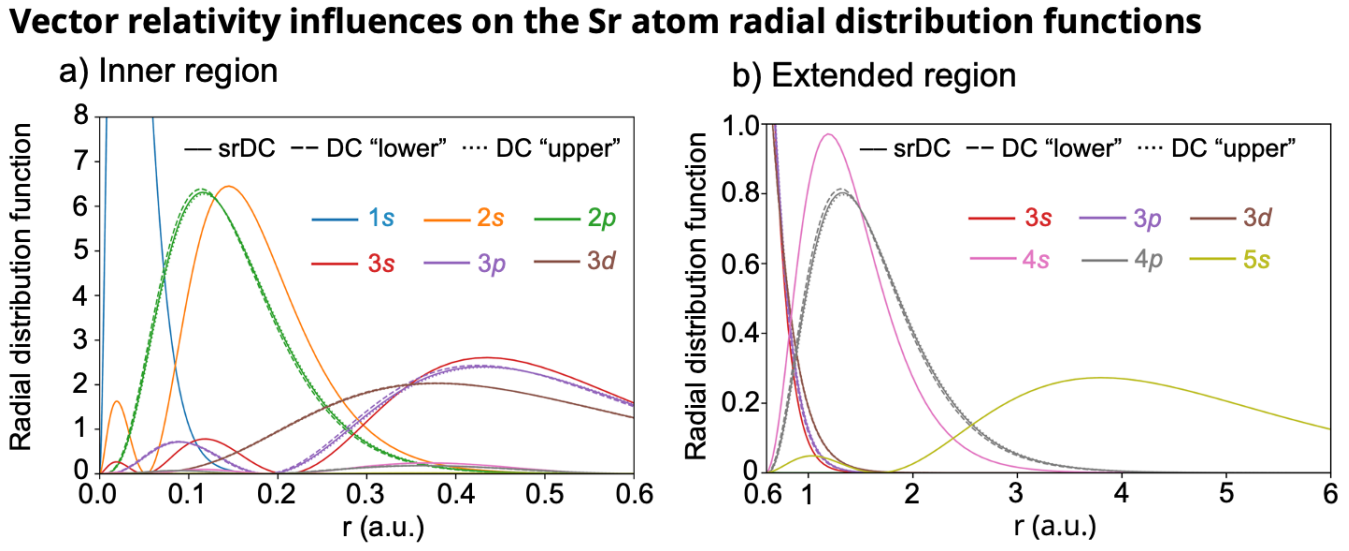

Figure S4 Orbital radial distribution functions for Sr atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

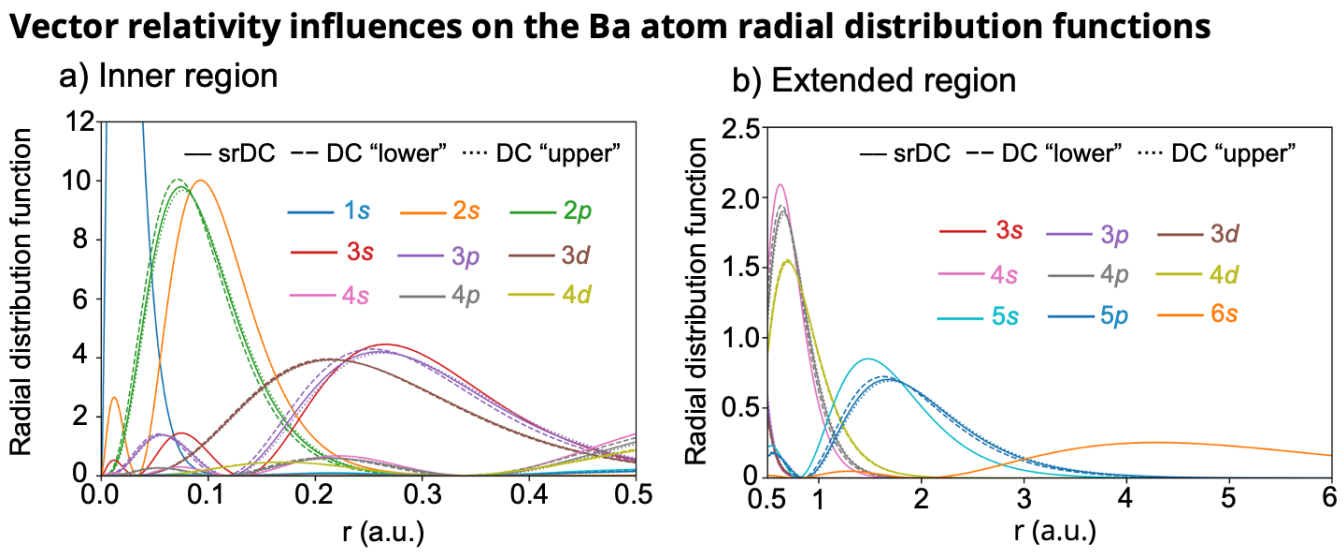

Figure S5 Orbital radial distribution functions for Ba atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

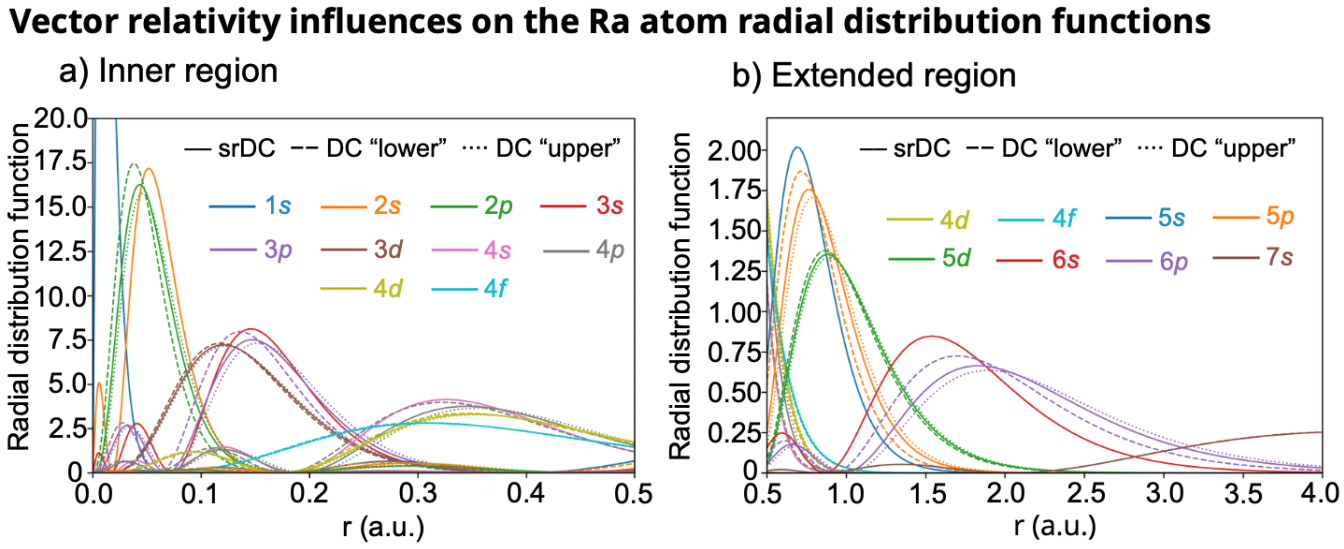

Figure S6 Orbital radial distribution functions for Ra atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

S5.2 p-block atoms

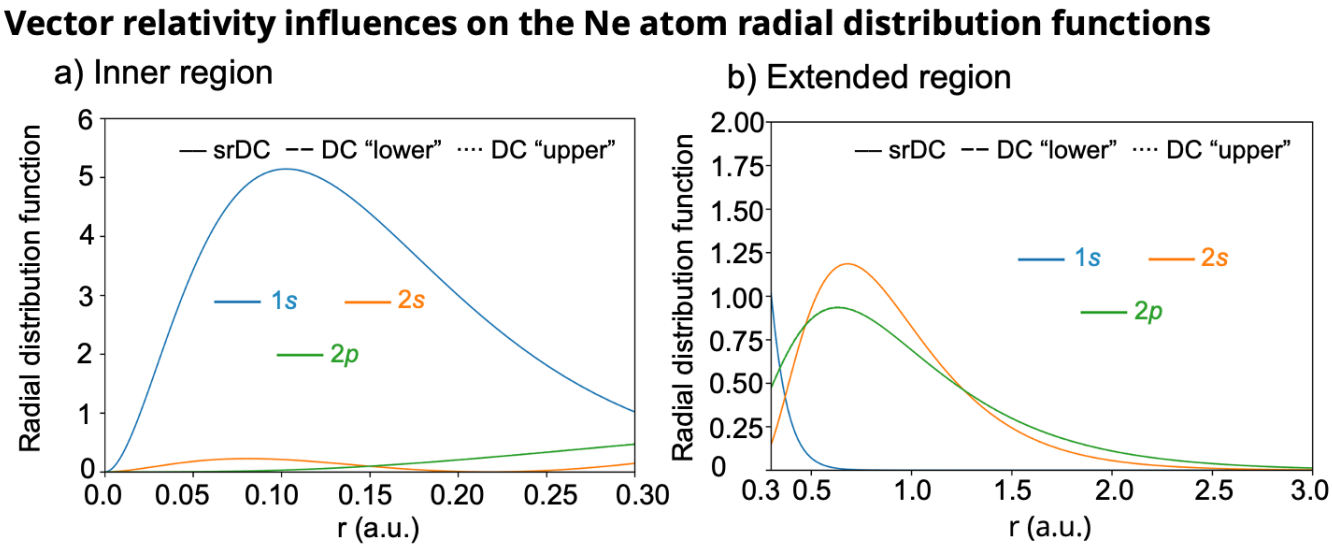

Figure S7 Orbital radial distribution functions for Ne atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

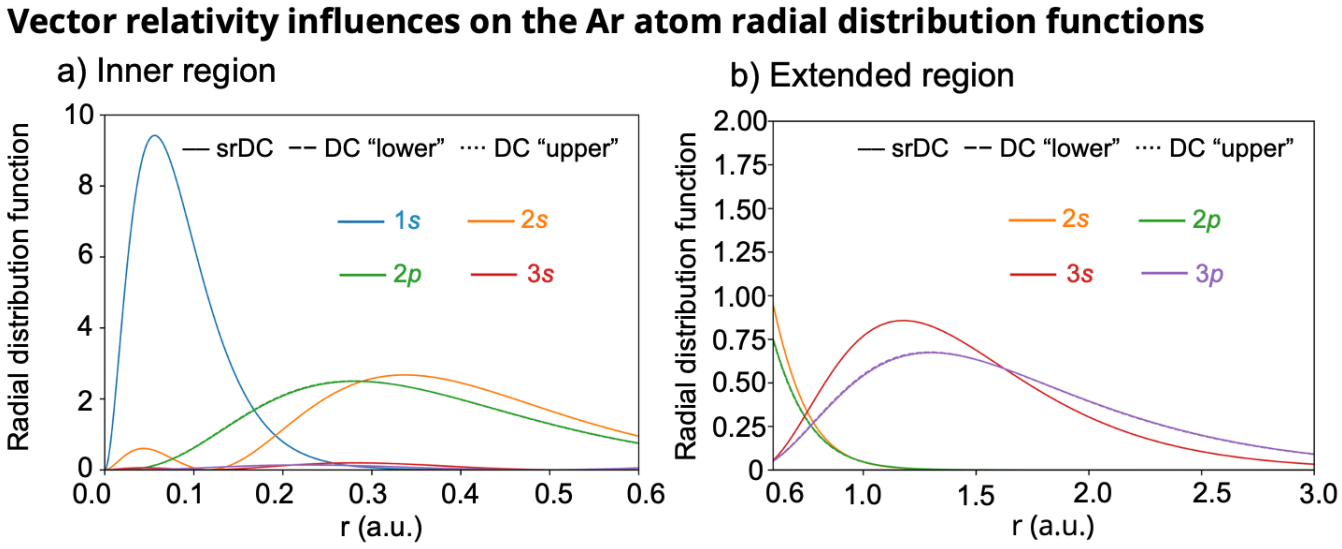

Figure S8 Orbital radial distribution functions for Ar atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

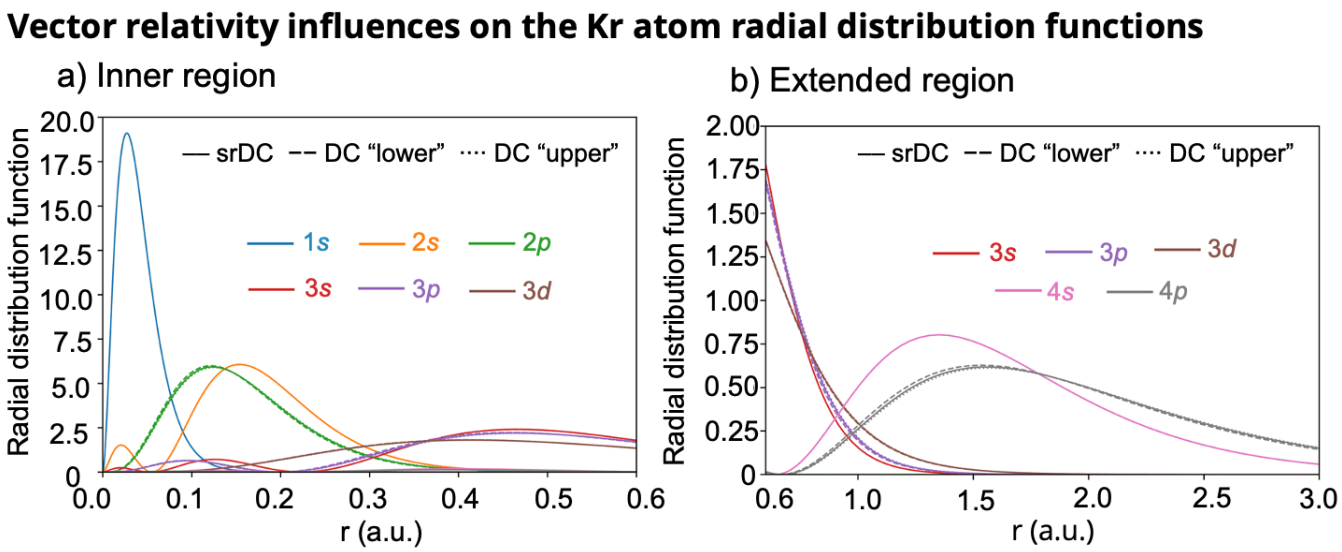

Figure S9 Orbital radial distribution functions for Kr atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

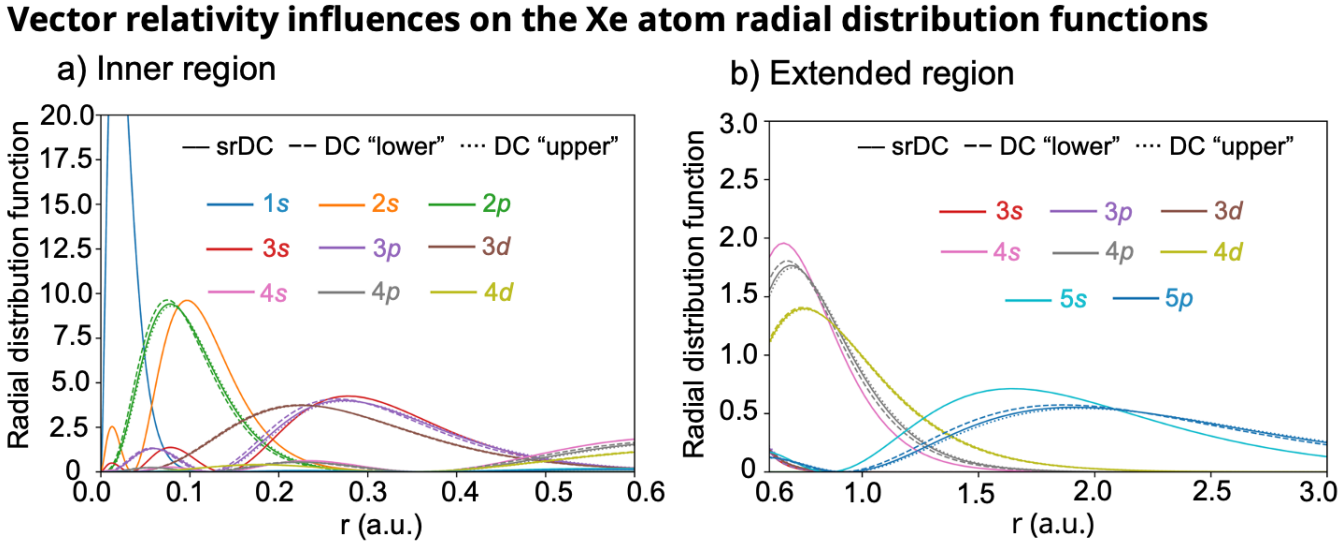

Figure S10 Orbital radial distribution functions for Xe atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

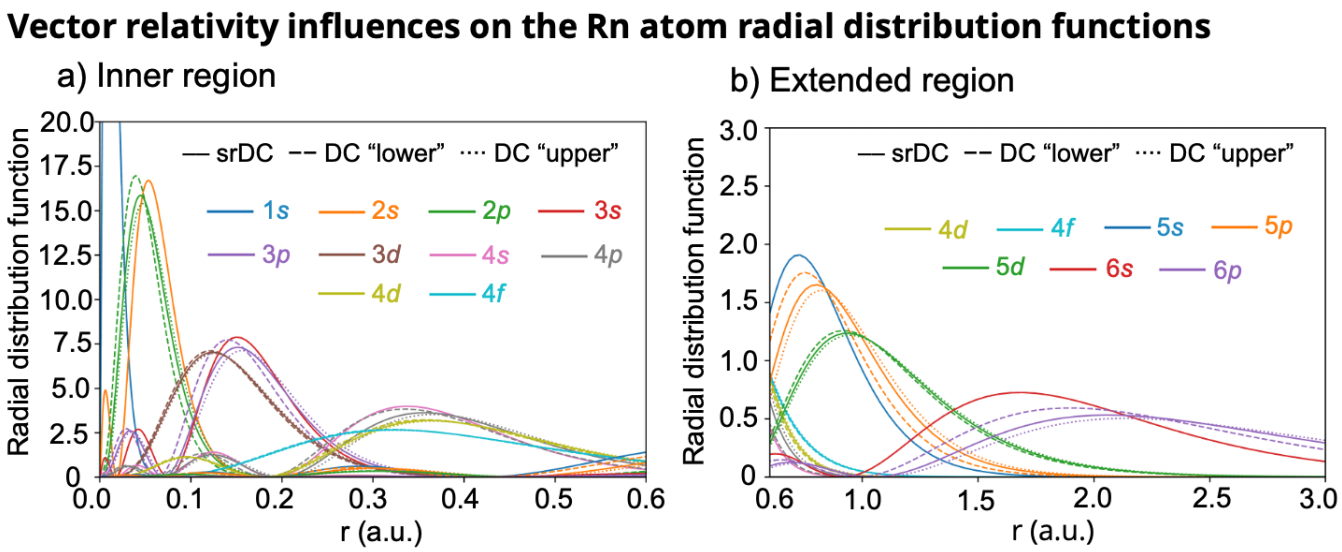

Figure S11 Orbital radial distribution functions for Rn atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

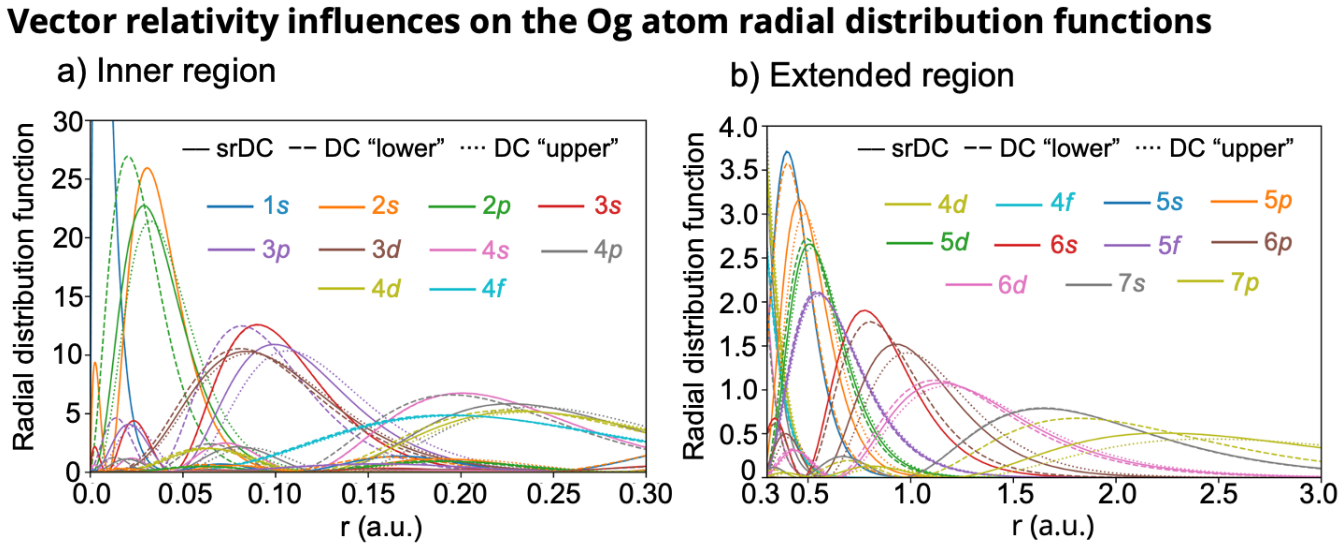

Figure S12 Orbital radial distribution functions for Og atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

S5.3 d-block atoms

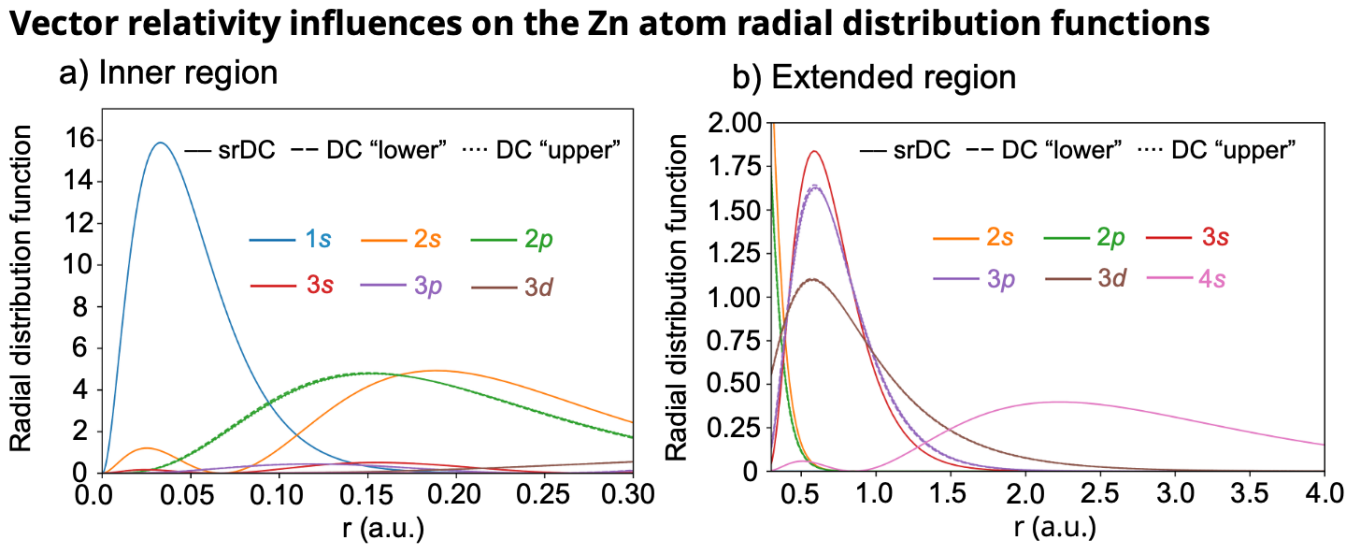

Figure S13 Orbital radial distribution functions for Zn atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

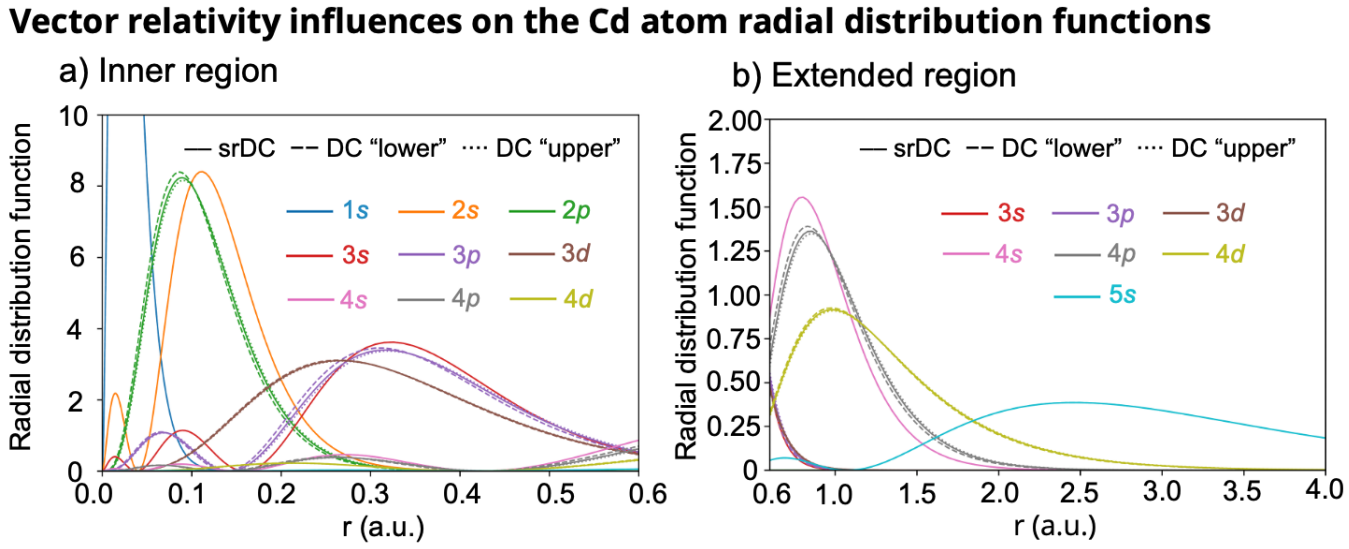

Figure S14 Orbital radial distribution functions for Cd atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

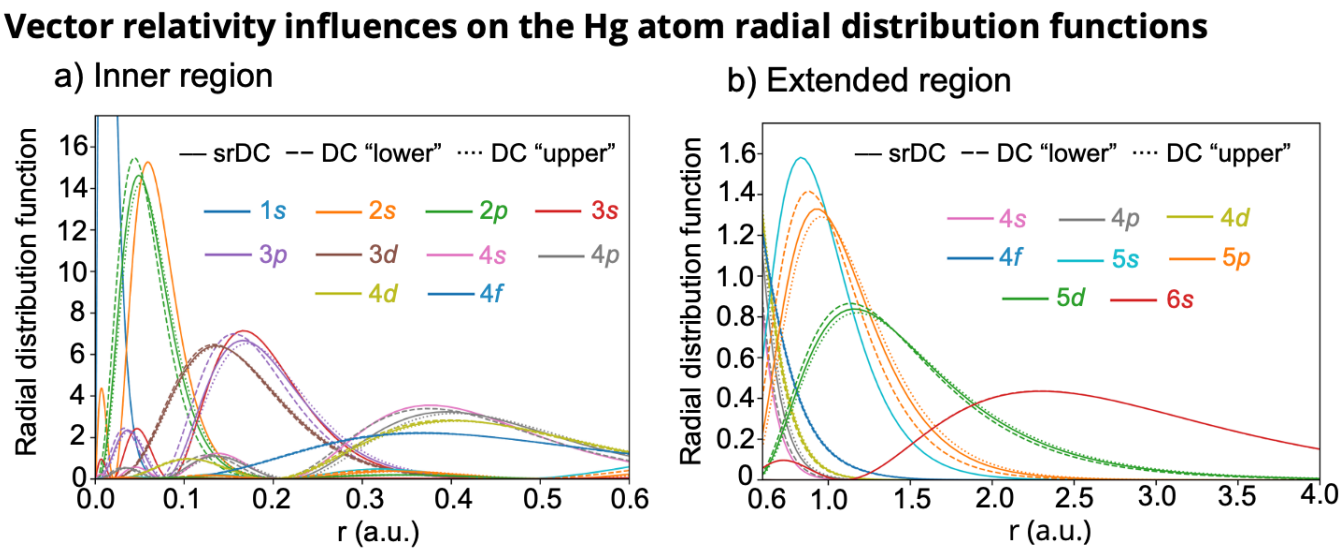

Figure S15 Orbital radial distribution functions for Hg atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

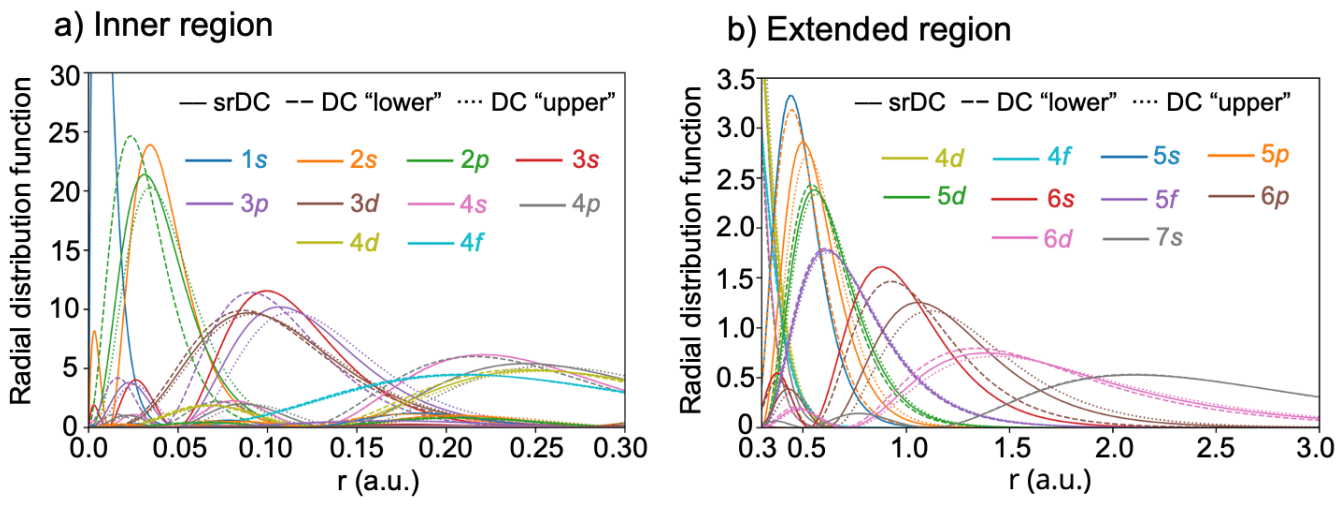

Figure S16 Orbital radial distribution functions for Cn atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

S5.4 f-block atoms

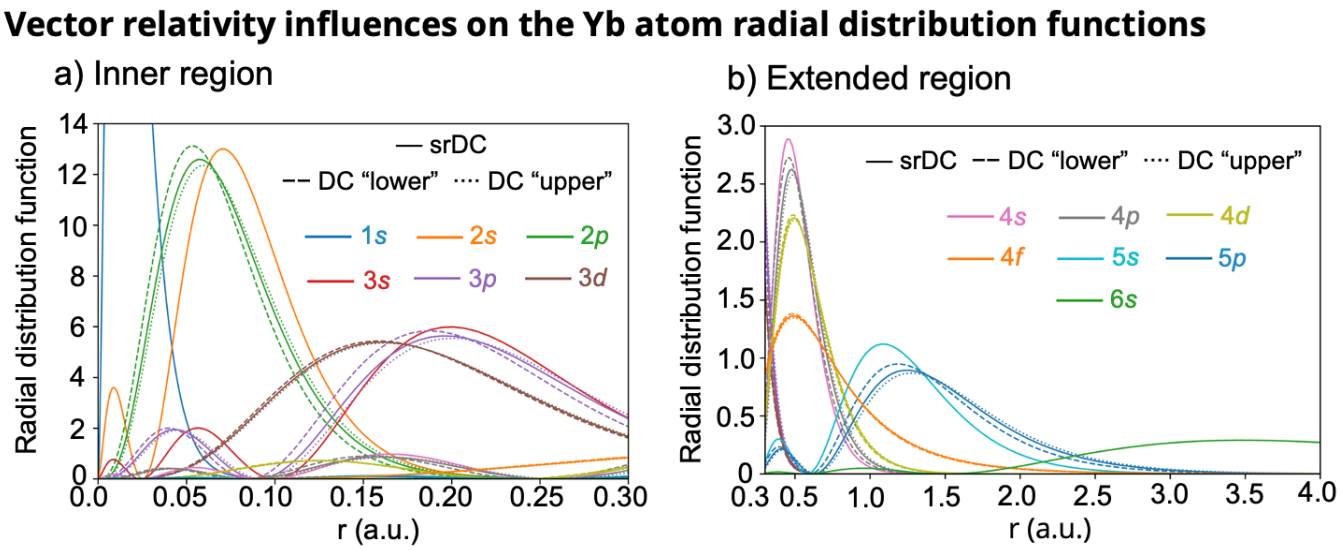

Figure S17 Orbital radial distribution functions for Yb atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).

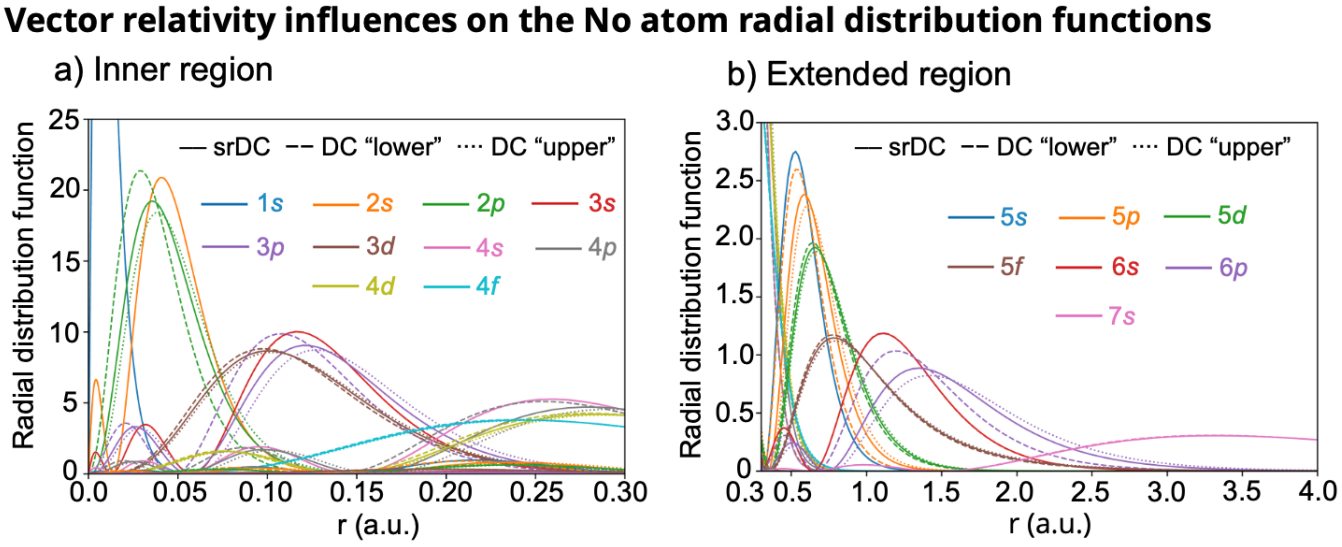

Figure S18 Orbital radial distribution functions for No atom with scalar-relativistic Dirac–Coulomb (srDC) and DC Hamiltonians over a) compact and b) expanded length ranges. The "lower" and "upper" designations refer to the magnitude of different j components of an orbital (e.g., "lower" for $2p$ is $2p_{1/2}$).