

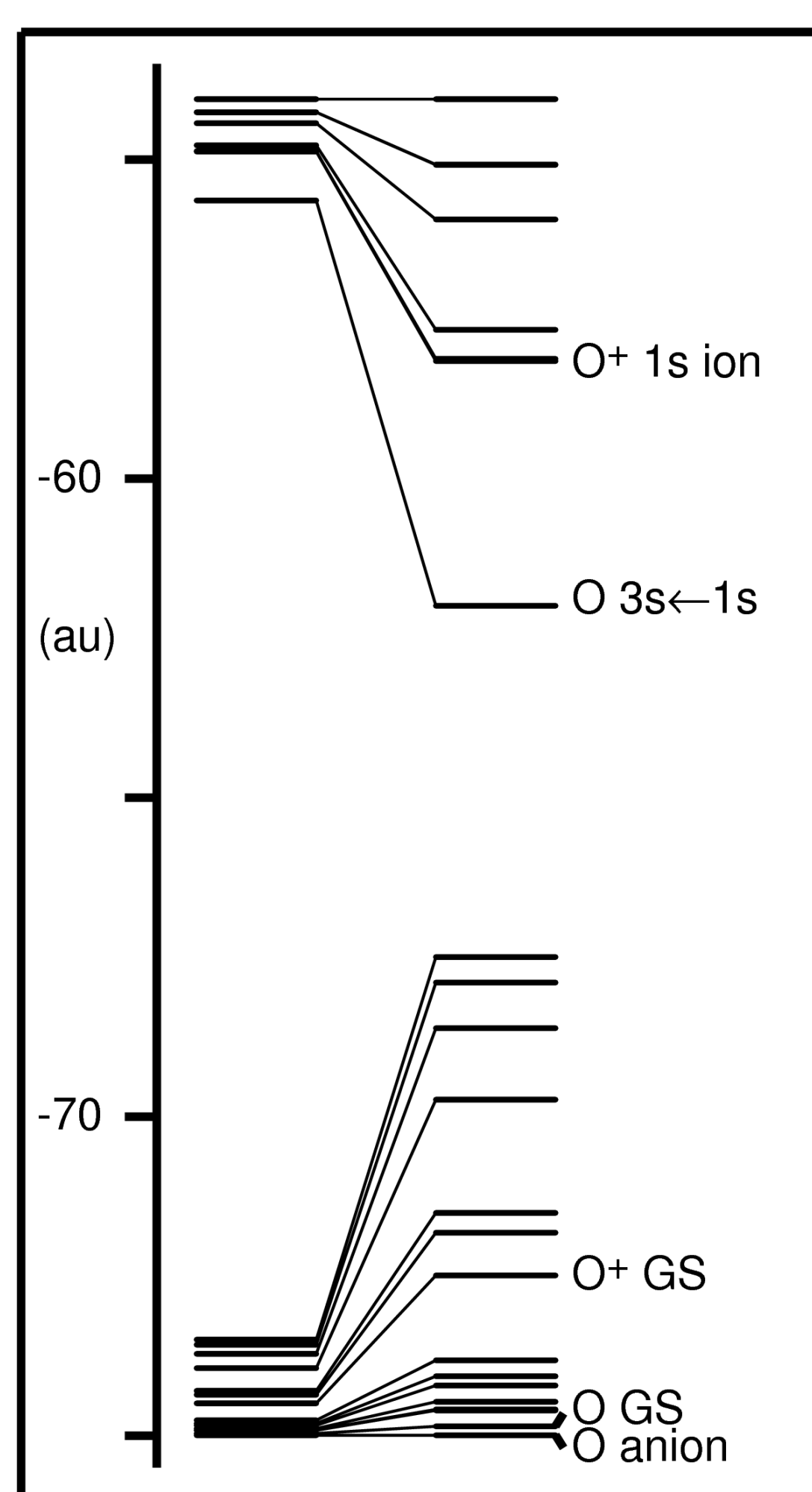
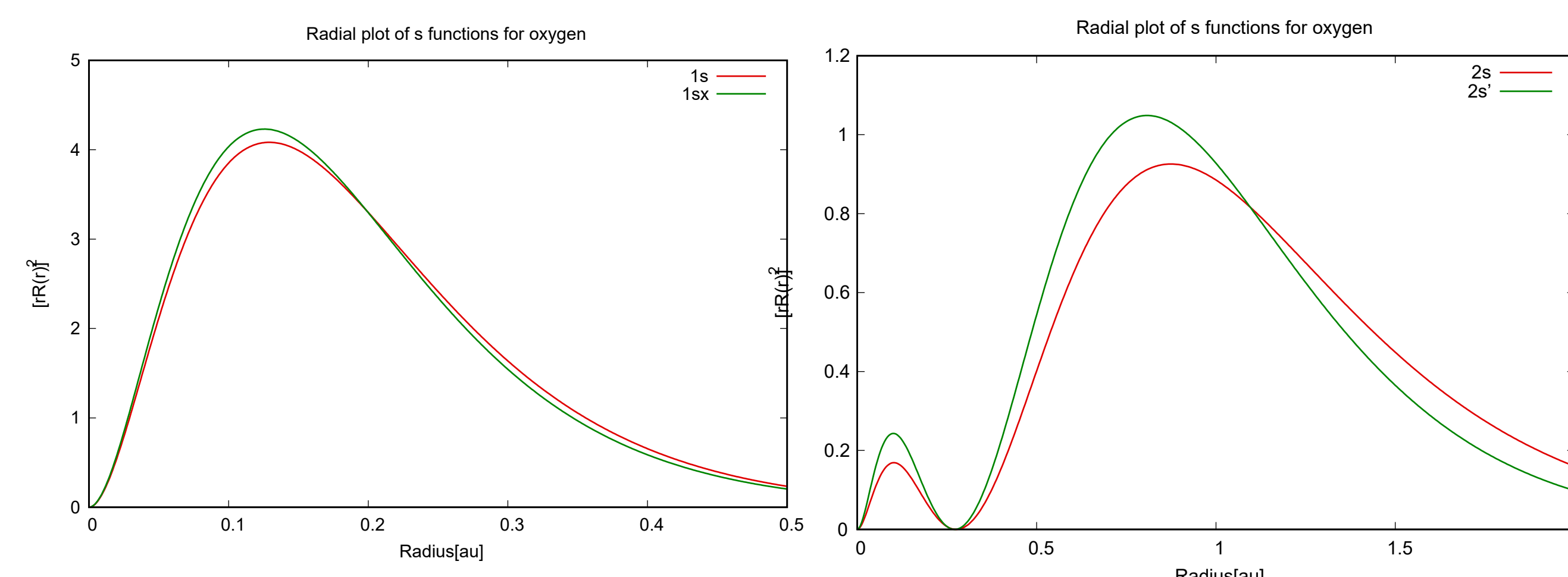
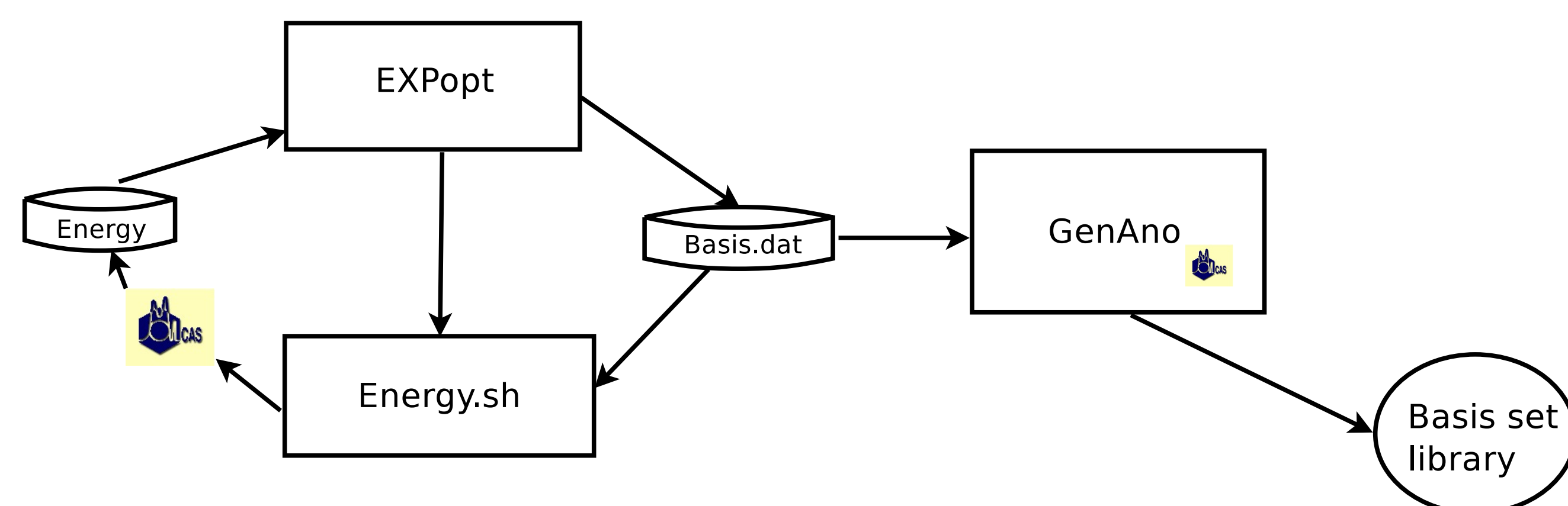
A generally-contracted Gaussian basis set for photochemistry and photophysics in the range 0-2 keV

Andreas Nyvang², Per Åke Malmqvist¹, Per-Olof Widmark¹, Valera Veryazov¹

¹Div. Theoretical chemistry, Lund University, Naturvetarvägen 14, Lund 22100, Sweden

²Department of Chemistry, Aarhus University, Langelandsgate 140, DK-8000 Aarhus C, Denmark

The recent availability of high resolution spectroscopy using synchrotron radiation makes it desirable to use conventional ab-initio quantum chemistry for studies of high-energy states, their evolution and subsequent radiative or non-radiative deexcitation, with the same methodology as is common for photochemical studies. Since the systems have several deep open shells, a multiconfigurational treatment is mandatory. The higher energy, together with a high demand on the accuracy, requires new basis sets to be developed.



Preliminary calculation for C, N, O, and F 1s cores, only, shows that standard contracted bases cannot represent the 1s and 1s² states with acceptable accuracy, but a small optimized basis (8s,5p) is accurate. Oxygen results: Energies (au) and errors

Basis	1s ¹	1s ¹ error	1s ²	1s ² error
ANO-L-VQZP	-31.9754	0.0246 (0.670 eV)	-59.1159	0.0407 (1.108 eV)
Optim. 8s5p	-31.9996	0.00039 (0.011 eV)	-59.1469	0.0097 (0.263 eV)
Exact	-32.0000	—	-59.15659512	—

Calculations using the preliminary contracted basis for CO and CH₄ show that improvements to the contraction coefficients are needed.

	CO	CH ₄
CASSCF (VDZ)	301.619	292.766
CASPT2 (VDZ)	-	292.991
CASSCF (Uncontracted)	298.163	290.504
CASPT2 (Uncontracted)	295.941	290.348
Experiment	296.069	290.707

States, excitation energies (eV), dipole and velocity transition strengths (1/ps), and polarization (Cs).

Excitations (RASSI)	Energy(eV)	Dipole	Velocity	Polarization
5a' ← 1a' (O1s)	537.2	0.124	0.139	A'
6a' ← 1a' (O1s)	539.1	0.316	0.289	A'
7a' ← 1a' (O1s)	539.8	0.065	0.052	A'
2a'' ← 1a' (O1s)	537.7	0.075	0.065	A''

Orbitals used for H₂O calculations. Starred orbitals are unoccupied in the ground state.

Starred are Valence/Rydberg orbitals. Orbitals, and orbital energies, for the ground state, and for the excited states (average, approximate).

1a'	2a'	3a'	4a'	5a'	6a'	7a'	1a''	2a''
-20.6	-1.36	-0.72	-0.59	0.03	0.03	0.04	-0.51	0.04
-21.3	-1.78	-1.13	-1.02	-0.07	-0.01	0.01	-0.97	0.01

A selection of results for the O atom, including states with 7-9 electrons, using a provisional ANO-like basis set. An active orbital set with 9s and 6p functions was used in the CASSCF.

Term symbol	CASSCF	CASPT2	Comment
9el 1s ² 2s ² 2p ⁵ (² P)	-74.99312814	-75.08869714	(a)
8el 1s ² 2s ² 2p ⁴ (³ P)	-74.96463166	-75.04338116	(b)
9el 1s ² 2s ² 2p ⁴ 3s ¹ (⁴ P)	-74.91505505	-75.00902335	
9el 1s ² 2s ² 2p ⁴ 3s ¹ (² P)	-74.91167484	-75.00621254	
8el 1s ² 2s ² 2p ⁴ (¹ D)	-74.88775183	-74.97024151	
9el 1s ² 2s ² 2p ⁴ 3s ¹ (² D)	-74.83732731	(Not done yet)	
8el 1s ² 2s ² 2p ⁴ (¹ S)	-74.80808692	(Not done yet)	(c)
9el 1s ² 2s ² 2p ⁴ 3s ¹ (² S)	-74.75782354	(Not done yet)	
7el 1s ² 2s ² 2p ³ (⁴ S)	-74.49232472	-74.55087895	
7el 1s ² 2s ² 2p ³ (² D)	-74.35849382	-74.42617522	
7el 1s ² 2s ² 2p ³ (² P)	-74.29644780	(Not done yet)	
7el 1s ² 2s ¹ 2p ⁴ (⁴ P)	-73.94069994	-74.00359392	
7el 1s ² 2s ¹ 2p ⁴ (² D)	-73.71717354	-73.79037341	
7el 1s ² 2s ¹ 2p ⁴ (² S)	-73.57397788	(Not done yet)	
7el 1s ² 2s ¹ 2p ⁴ (² P)	-73.49443457	(Not done yet)	
8 el 1s ¹ 2s ² 2p ⁵ (³ P)	-55.64141746	-55.70411149	
7 el 1s ¹ 2s ¹ 2p ⁴ (² D)	-54.87445538	-54.92598460	(d)
7 el 1s ¹ 2s ¹ 2p ⁴ (² P)	-54.86668837	(Not done yet)	
7 el 1s ¹ 2s ¹ 2p ⁴ (² S)	-54.77616853	(Not done yet)	
7 el 1s ¹ 2s ¹ 2p ⁵ (⁴ P)	-54.43083485	-54.47880298	
7 el 1s ¹ 2s ¹ 2p ⁵ (² P)	-54.25869418	-54.30934358	
7 el 1s ¹ 2s ¹ 2p ⁵ (² P)	-54.25778584	-54.31199442	
7 el 1s ¹ 2s ¹ 2p ⁵ (² P)	-54.05271682	(Not done yet)	

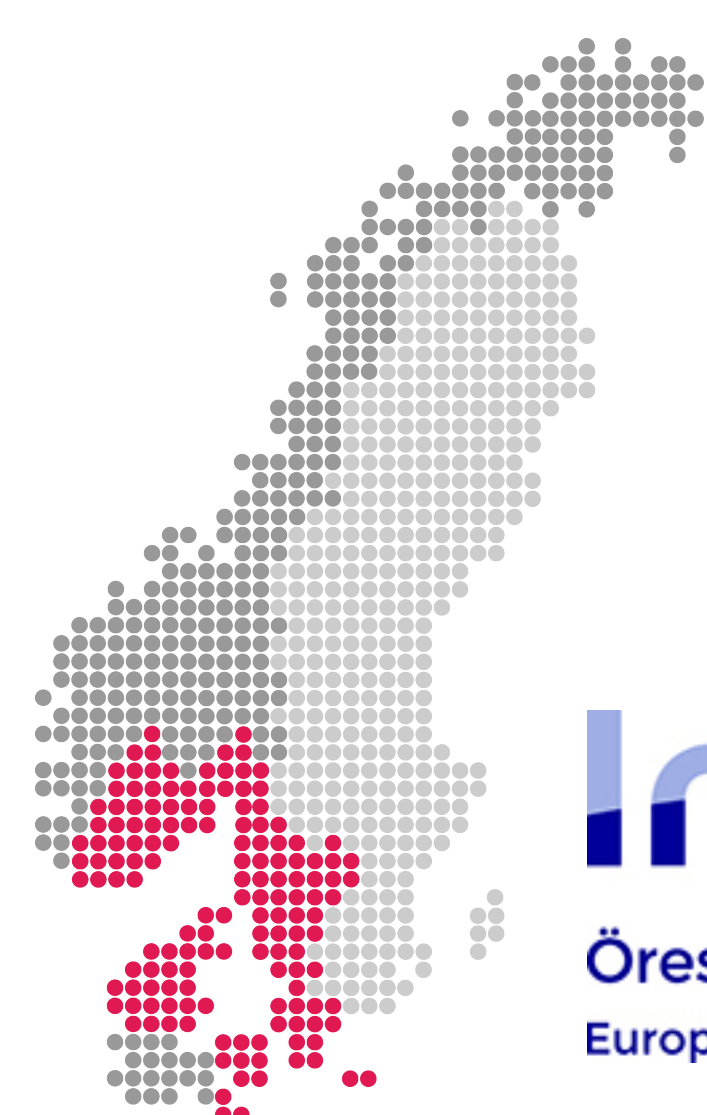
a: E.A. 0.04531598 a.u., 1.233 eV. Exp: 1.461 eV.
 b: G.S. Experimental total binding energy: 75.1083825
 c: I.P. 0.49250221 a.u., 13.40 eV. Exp: 13.62 eV.
 d: I.P. 20.11739656 a.u., 547.43 eV. Exp:

This diagram shows, in the left, accurate energies of a number of states of the O atom and ions. The levels are clustered around energies of -75 Eh and -54 Eh. The expanded parts on the right is annotating some of the states. Those at -54 Eh have one electron excited out from the core, and the difference of 20 Eh corresponds to about 540 eV. All the states cannot easily be treated with a common set of orbitals, but that is not a problem when using the RASSI facility of Molcas. However, the basis set must be specially design to handle the core excited/ionized states.

Checking a specially designed basis set against a conventional basis, and against accurate data for the 1s¹ and 1s² states of C, N, O, and F show that it is fairly easy to get accurate results with only a small basis, if optimized for the purpose

In order to compute the wave functions for the core excited states, we modified CASSCF to use a projector of doubly-occupied core states, and shifting the Hamiltonian.

The project is a collaboration between the universities of Lund and of Aarhus, and was sponsored by grant AU-007 from MAX4ESSFUN



Interreg
Öresund-Kattegat-Skagerrak
European Regional Development Fund



AARHUS UNIVERSITY

