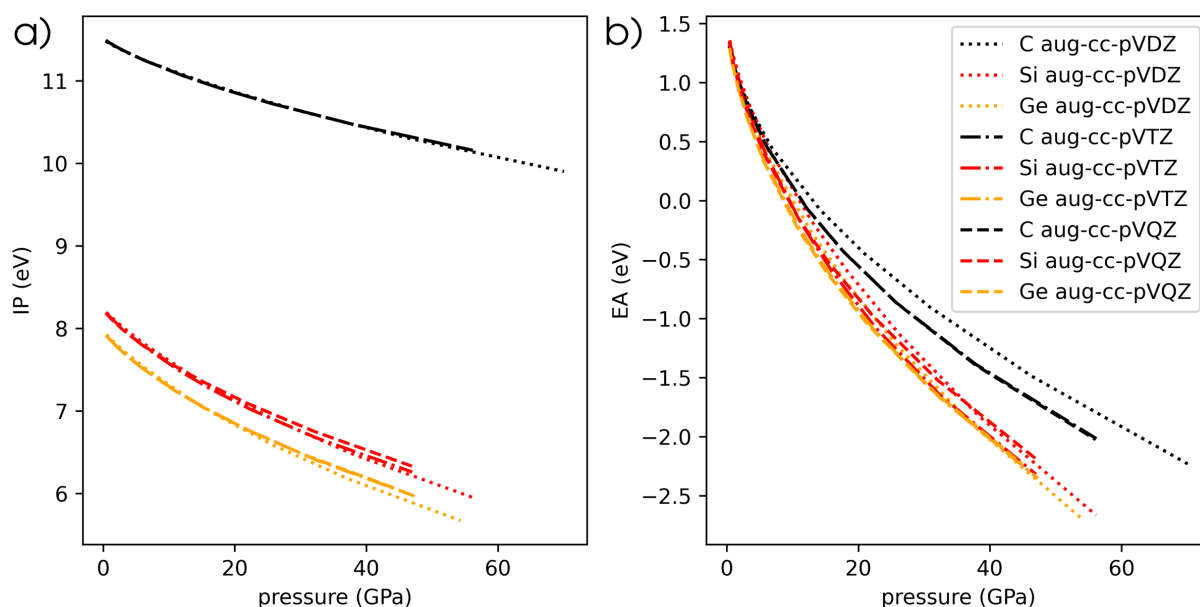


## Conceptual Density Functional Theory under Pressure: Part I. XP-PCM Method Applied to Atoms: Supporting Information

### 1. Reliability of the functional, basis set and barrier hardness evaluated on 3 group IVa elements.

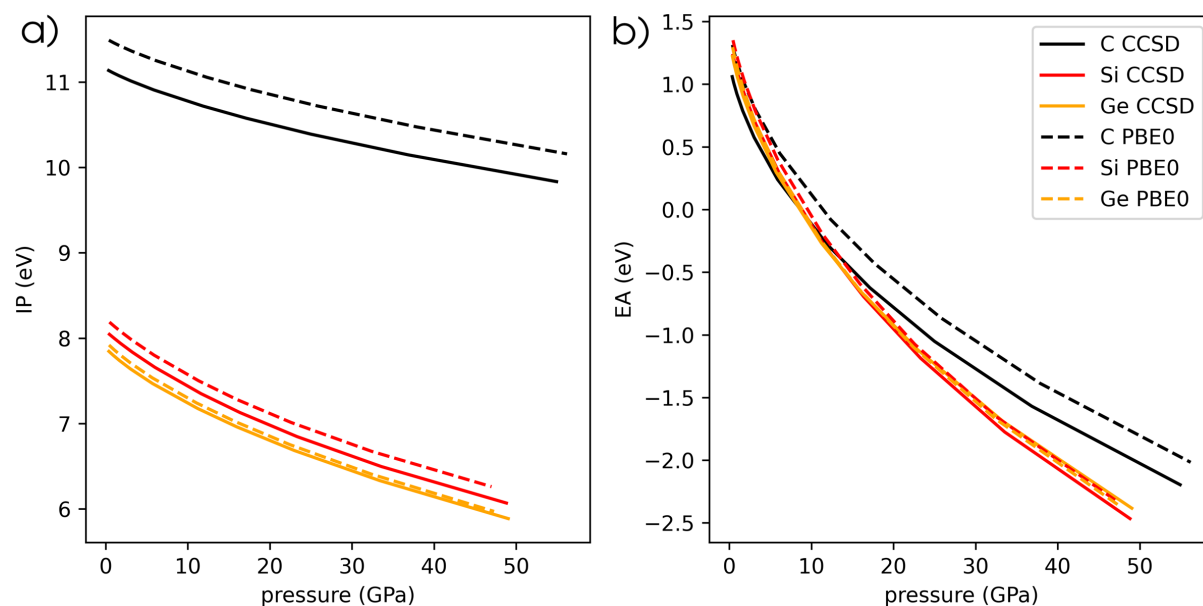
The influence of the employed basis set on the results is examined by comparing 3 levels of the Dunning augmented and polarized basis set (i.e. aug-cc-pVDZ, aug-cc-pVTZ & aug-cc-pVQZ) at the DFT/PBE0 level of theory for the ionization potential and electron affinity for 3 group IVa elements (C, Si & Ge) under pressure. While the aug-cc-pVDZ basis set gives similar results at ambient conditions, its behavior at high pressure starts deviating from the triple and quadruple zeta basis sets. The aug-cc-pVTZ and aug-cc-pVQZ sets however, perform very similarly for both the ionization potential and electron affinity, indicating the triple zeta level to be a reliable choice for the subsequent work.



**Figure S1:** a) Ionization potential and b) electron affinity under pressure for C, Si and Ge using the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets and PBE0 exchange-correlation functional.

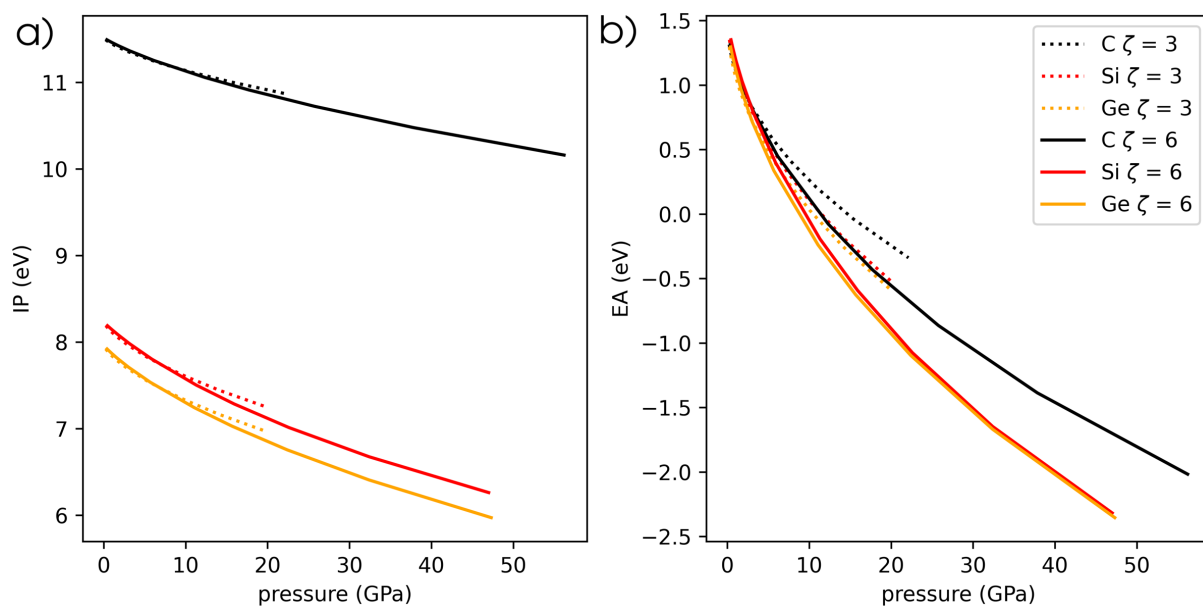
To assess the performance of the chosen exchange-correlation functional, the behavior of the (isochoric) ionization potential and electron affinity are considered for carbon, silicon and germanium using both the PBE0 exchange-correlation functional and the CCSD method with the aug-cc-pVTZ basis set. The PBE0 functional was chosen because of its prior use in the determination of electronegativities under pressure [M. Rahm, Cammi, R., Ashcroft, N. W., Hoffmann, R., J. Am. Chem. Soc., 2019, 141, 10253-10271.], its ability to reproduce experimental ionization potentials and electron affinities at ambient conditions and good quality relative to other common functionals [M.G. Medvedev, Bushmarinov, I.S., Sun, J., Perdew, J.P., Lyssenko, K.A., Science, 2017, 355, 49-52.]. This shows an error

on the value of IP and EA which remains roughly constant and reasonably small over the entire pressure range considered, which merits the use of the PBE0 functional in the remainder of this work.



**Figure S2:** a) Ionization potential and b) electron affinity under pressure for C, Si and Ge using the CCSD/aug-cc-pVTZ and PBE0/aug-cc-pVTZ levels of theory.

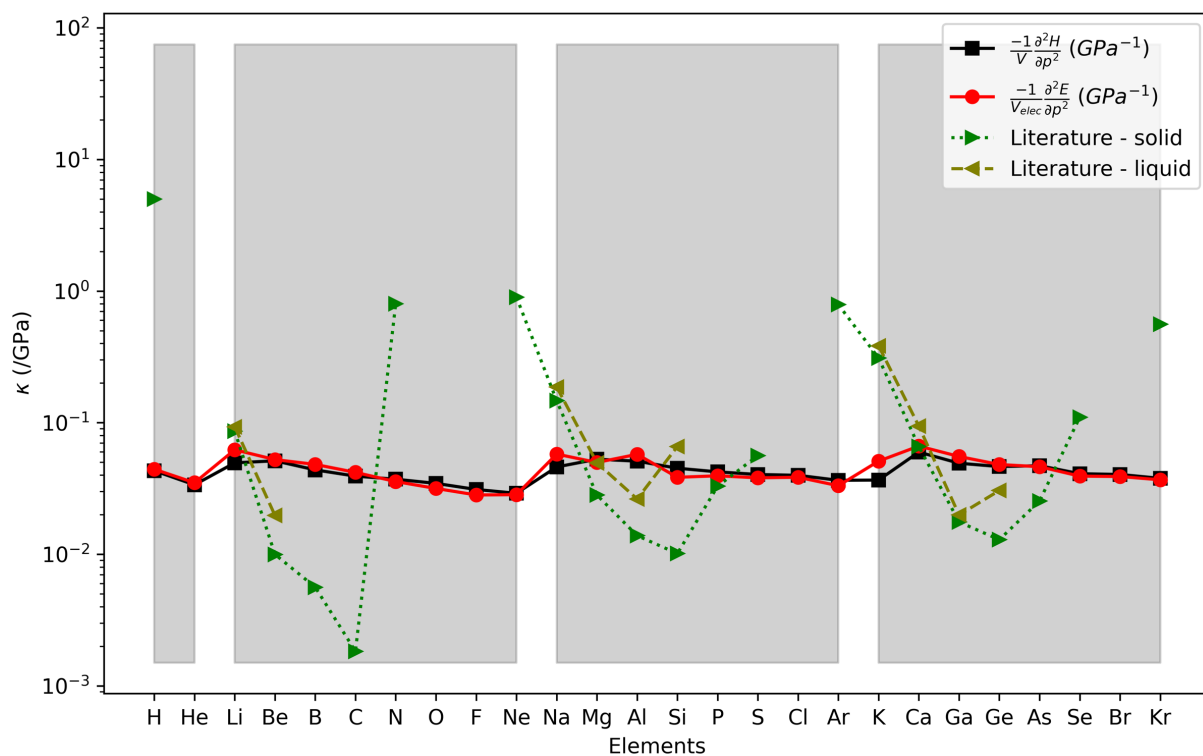
Finally, the value of the barrier hardness in XP-PCM is a semi-empirical constant, characteristic for the inert solvent environment. Generally, a choice of 3, 6 or 9 is suggested as appropriate for this parameter and the popular choice for a value of 6 (e.g. validated in [Rahm, M., Cammi, R., Ashcroft, N.W., Hoffmann, R., 2019, J. Am. Chem. Soc., 141, p.10253-10271]) is retained in the present work. Nevertheless, the effect of  $\zeta$  is investigated by comparing the results for the IP and EA with a value of 3 and 6 as the barrier hardness. This shows for 3 group IVA elements that the evolution of the IP and EA with pressure is fairly independent of the parameter choice at the lower end of the pressure range. On the other end of our considered pressure range, one finds a systematically reduced effect due to the pressure resulting in lower pressures for similar cavity scaling factors, owing to the reduced Pauli-repulsion barrier.



**Figure S3:** a) Ionization potential and b) electron affinity under pressure for C, Si and Ge using two different values of the barrier hardness (3 & 6) at the PBE0/aug-cc-pVTZ level of theory.

## 2. Atomic Compressibility

The atomic compressibility based on the enthalpy and energy (electronic) are provided in the figure below and compared to experimental measurements of isothermal compressibilities on solids and liquids at their melting point.

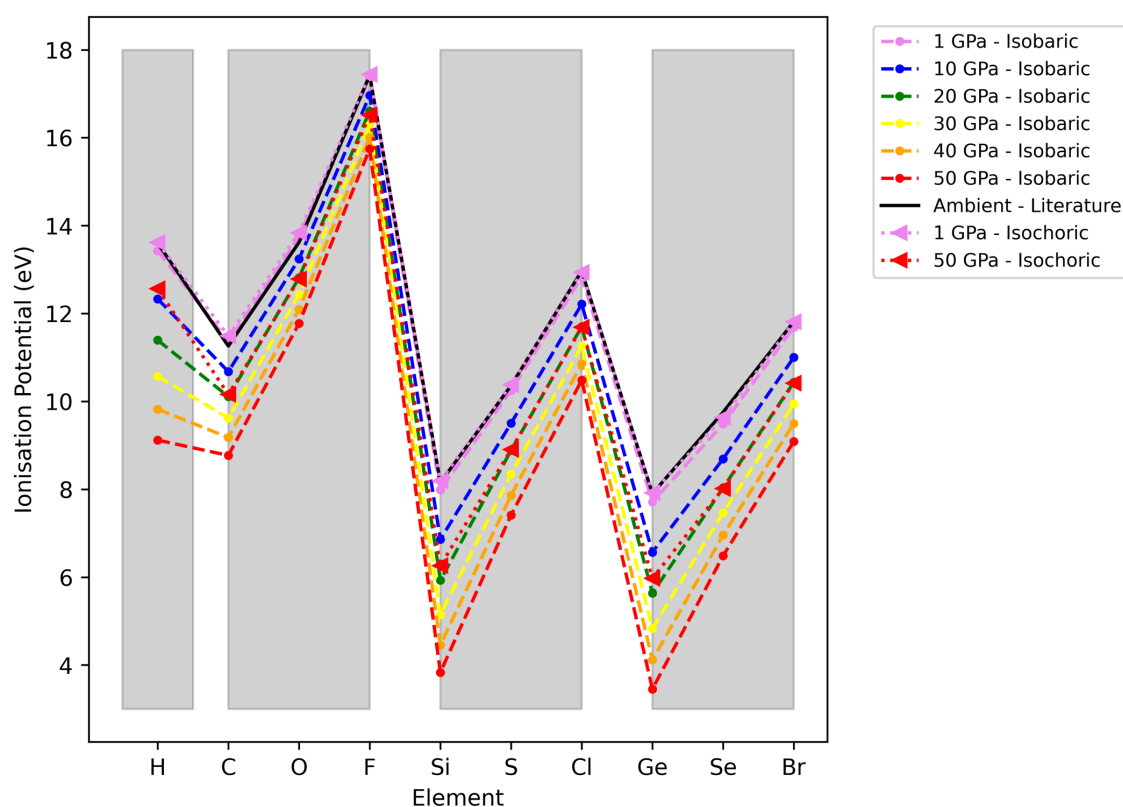


**Figure S4:** Electronic (red) and enthalpic (black) compressibility of the main group elements hydrogen to krypton. Additional literature values for solids and liquids are provided. Grey zones group elements within one period of the periodic table.

Literature data were obtained from C. Kittel, Introduction to Solid State Physics, 2005, 8<sup>th</sup> ed., Hoboken, John Wiley & Sons, Inc, p.52 and Y., Marcus, J. Chem. Thermodynamics, 2017, 109, 11-15.

### 3. Isobaric method for computing ionization energy and electron affinity

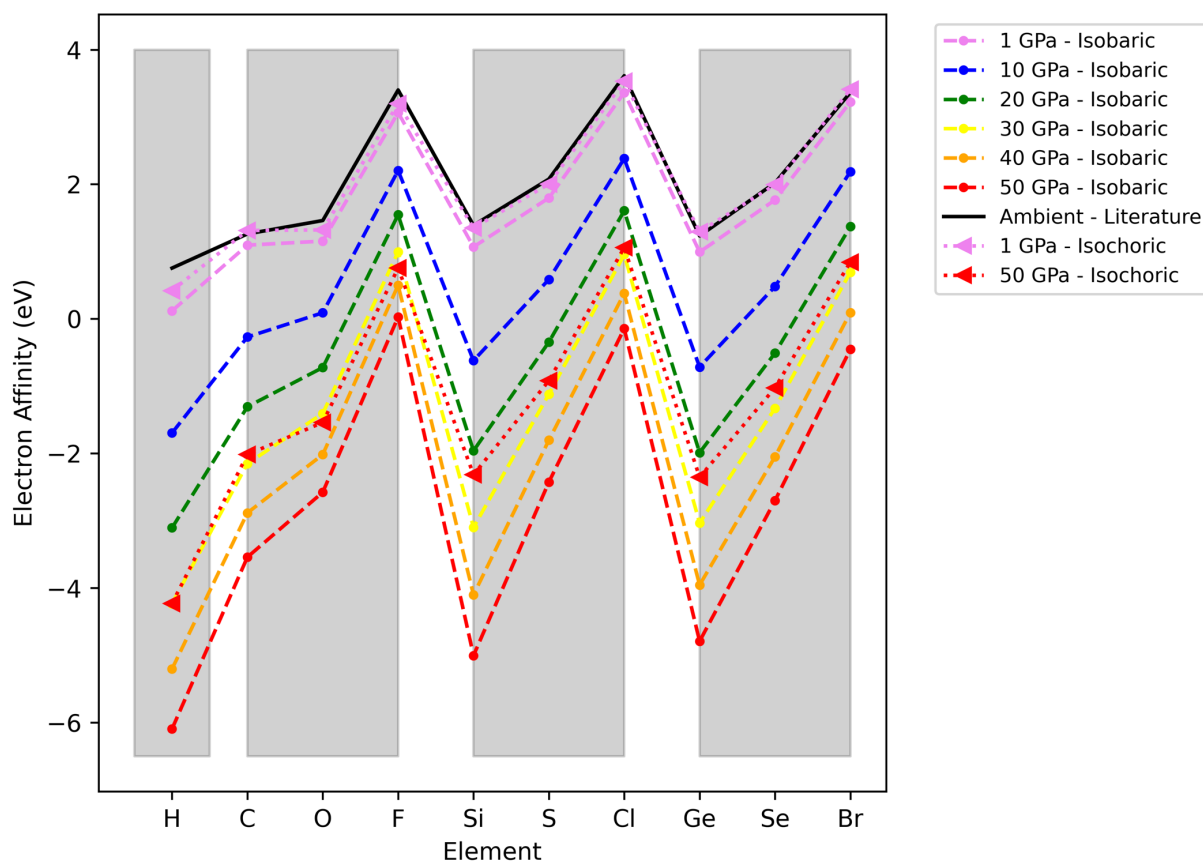
Next to the isochoric method described in the main text, an isobaric expansion of Equation 17 is possible in which the P constraint on different descriptors is an implicit one. Due to the isobaric nature of this method, we chose to include here the cavitation correction in Equation 16, thus obtaining derivatives of the type  $\left(\frac{\partial H}{\partial p}\right)^\pm$ . Computationally, this method adjusts the cavity volume of the ionic species to simulate the same pressure as the neutral species (Figure 1b in main text) and finds similar trends as for the isochoric ionization potential, provided in the figure below. In this figure, literature data were obtained from the NIST database. The isobaric properties were calculated for the selection of elements for which the Rahm monoanionic radii [M. Rahm, Hoffmann, R., Ashcroft, N.W., *Chem. Eur. J.*, 2016, **22**, 14625-14632] are available (*vide infra*). It is noted that the isobaric method generally results in lower ionization potentials than the isochoric method.



**Figure S5:** Isobaric ionization potential at different pressures for a selection of ten main group elements. Isochoric values at 1 and 50 GPa and experimental literature data are additionally provided. Grey zones group elements within one period of the periodic table.

In the figure below, the isobaric electron affinities are displayed for those elements with documented monoanionic Rahm radii [M. Rahm, Hoffmann, R., Ashcroft, N.W., *Chem. Eur. J.*, 2016, **22**, 14625-14632] and similar trends as for the isochoric electron affinities are obtained. Analogous to the isochoric ionization potential, a cavity contribution is introduced, associated to the transition from the neutral to the anionic cavity at a certain pressure. A steeper decrease of the electron

affinity under the effect of pressure is found for the isobaric method compared to the isochoric electron affinities.



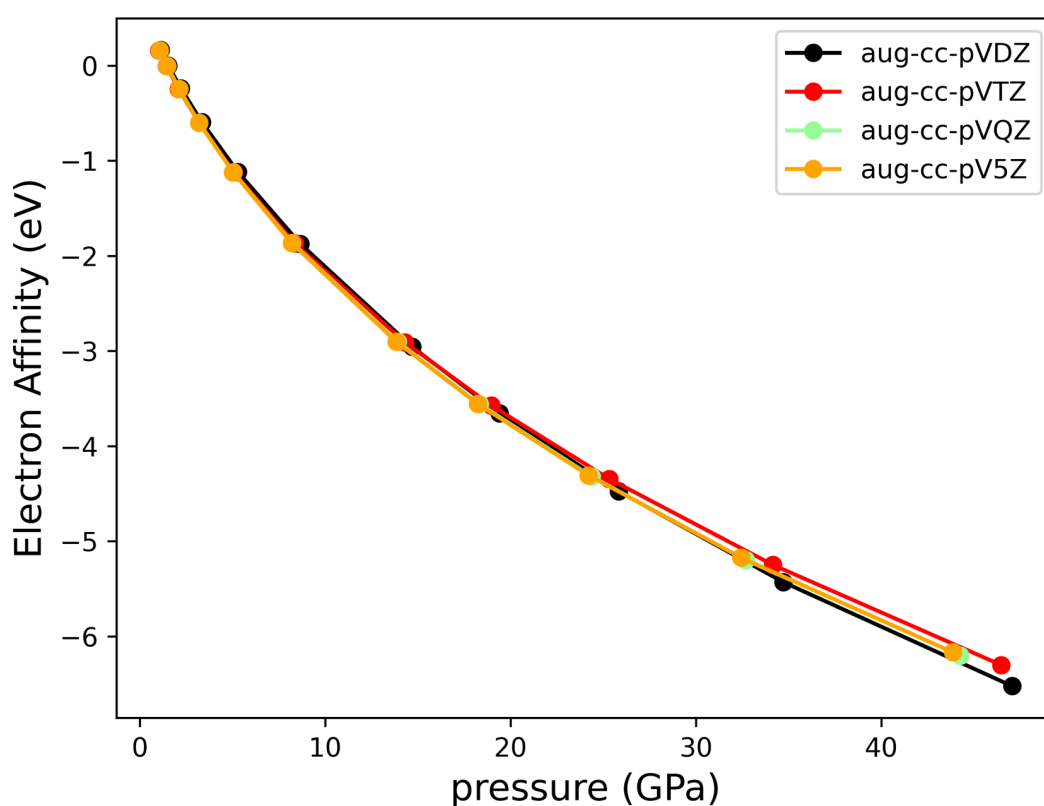
**Figure S6:** Isobaric electron affinities at different pressures for a selection of ten main group elements. Isochoric values at 1 and 50 GPa and experimental literature data are additionally provided. Grey zones group elements within one period of the periodic table.

Literature data were obtained from:

1. Bresteau, Drag, C., Blondel, C., *Phys. Rev. A*, 2016, 93.
2. C. Blondel, Delsart, C., Goldfarb, F., *J. Phys. B: At. Mol. Opt. Phys.*, 2001, 34, 281-288.
3. W. Chaibi, Peláez, R.J., Blondel, C., Drag, C., Delsart, C., *Eur. Phys. J. D*, 2010, 58, 29-37.
4. C. Blondel, Cacciani, P., Delsart, C., Trainham, R., *Phys. Rev. A*, 1989, 40, 3698-3701.
5. U. Berzinsh, Gustafsson, M., Hanstorp, D., Klinkmüller, A., Ljungblad, U., Mårtensson-Pendrill, A.M., *Phys. Rev. A*, 1995, 51, 231-238.
6. D. Bresteau, Babilotte, P., Drag, C., Blondel, C., *J. Phys. B: Atom. Molec. Opt. Phys.*, 2015, 48.
7. M. Vandevraye, Drag, C., Blondel, C., *Phys. Rev. A*, 2012, 85.

#### 4. Basis Set Stability of Electron Affinity

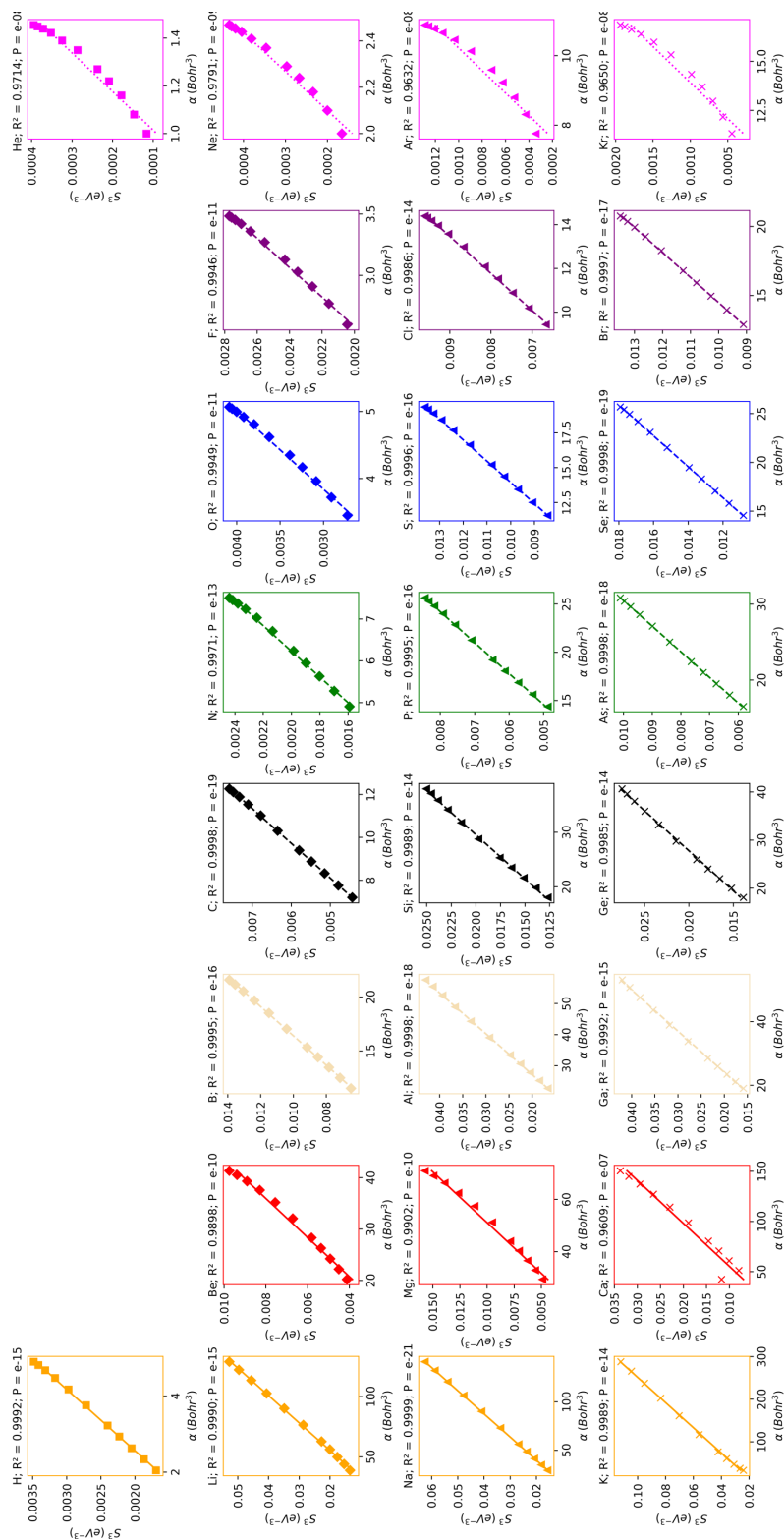
A common problem that is encountered when calculating negative electron affinities is the instability of the value with respect to a larger basis set. This is due to the fact that a larger basis can allow the electron to be described as fully separated from the atom, yielding a value of zero for the complete basis limit. For this reason, a lithium atom is tested as an example for stability by systematically increasing the basis set size from aug-cc-pVDZ to aug-cc-pV5Z. This shows that even when encountering negative electron affinities, stable values of the EA are obtained, independent of the basis size. Small deviations in the obtained pressure do occur, although these are still minor compared to other sources of error, e.g. choice of f-values and fitting procedure.



**Figure S7:** Electron affinity of a lithium atom under pressure using the aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ & aug-cc-pV5Z basis sets.

## 5. Correlation of Softness and Isotropic Polarizability for Atoms under Pressure

Individual plots of the correlation between the cube of the chemical softness and the isotropic polarizability for the main group elements from hydrogen to krypton. Generally good correlations are obtained for all elements and Pearson R<sup>2</sup> and P-values of the slope are provided for each element.



**Figure S8:** Correlation plots of the isotropic polarizability and cube of the softness of atoms for the main group elements of hydrogen to krypton.



## 6. Relative Destabilization of Orbital Energies

Individual plots of the relative destabilization  $\left(100\% \cdot \frac{\epsilon_i^p - \epsilon_i^{ref}}{\epsilon_i^{ref}}\right)$  compared to reference conditions (f=1.3) of the occupied orbital energies for the main group elements from lithium to krypton.

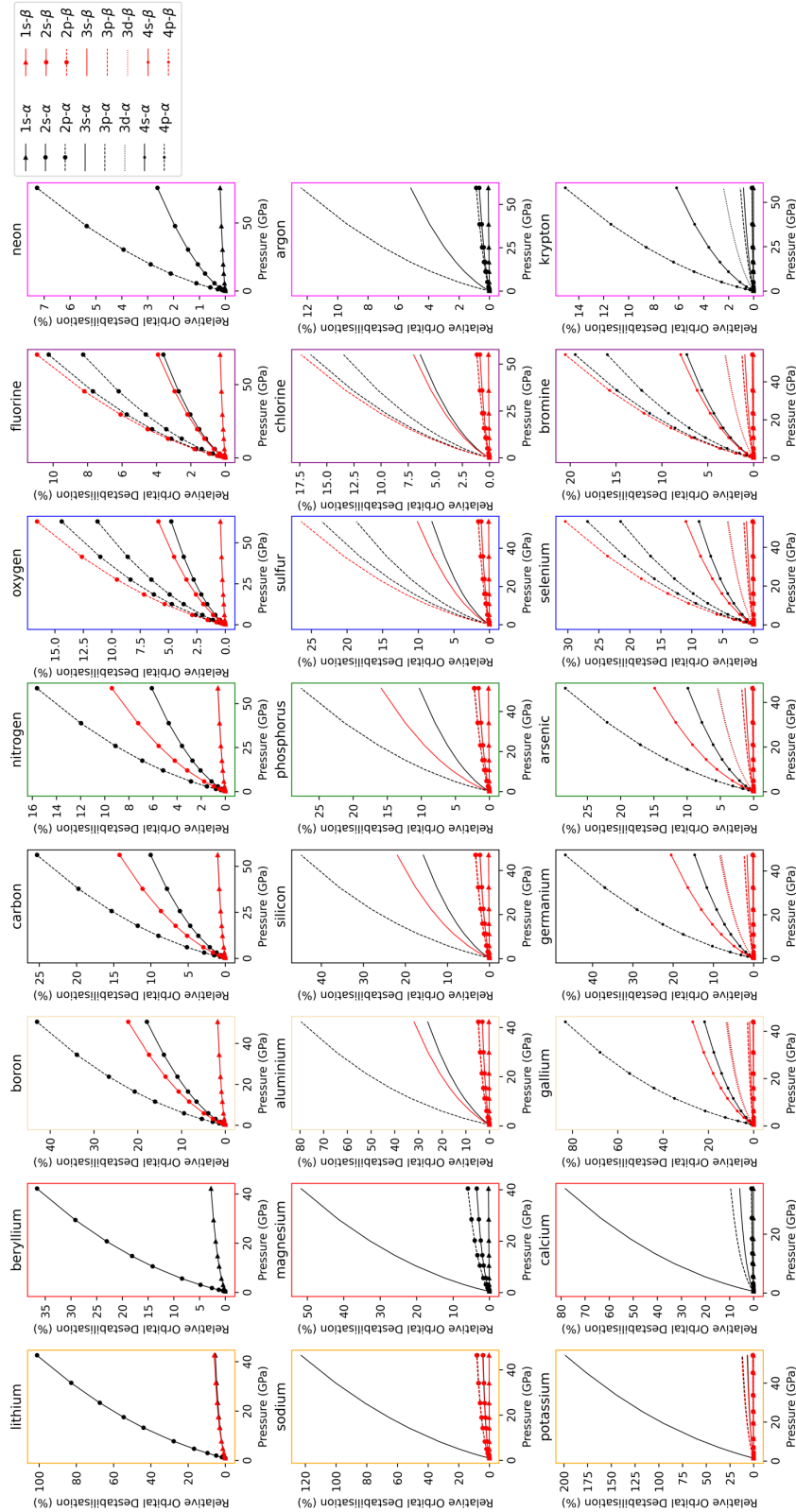
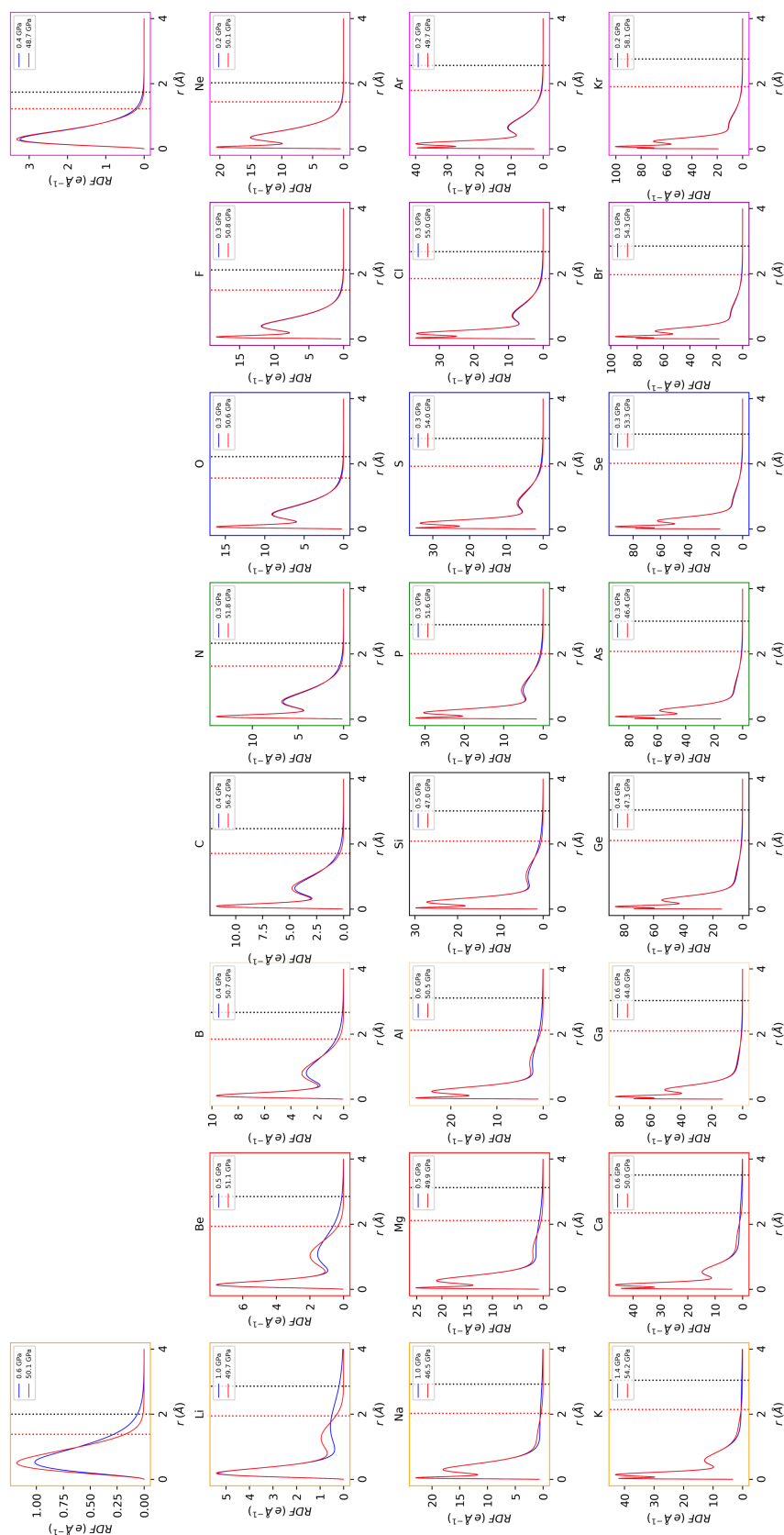


Figure S9: Relative orbital destabilizations of atoms under pressure for the main group elements from hydrogen to krypton.

## 7. Radial Distribution Function of Elements under Pressure

Individual plots of the radial distribution function of the main group elements from hydrogen to krypton at reference conditions ( $f=1.3$ ) and approximately 50 GPa.



**Figure S10:** Radial Distribution Functions (RDF) of atoms at  $\sim 1$  and  $\sim 50$  GPa for the main group elements from hydrogen to krypton.

## 8. Difference in Radial Distribution of Elements under Pressure

Individual plots of the difference in radial distribution function of the main group elements from hydrogen to krypton between reference conditions ( $f=1.3$ ) and approximately 50 GPa.

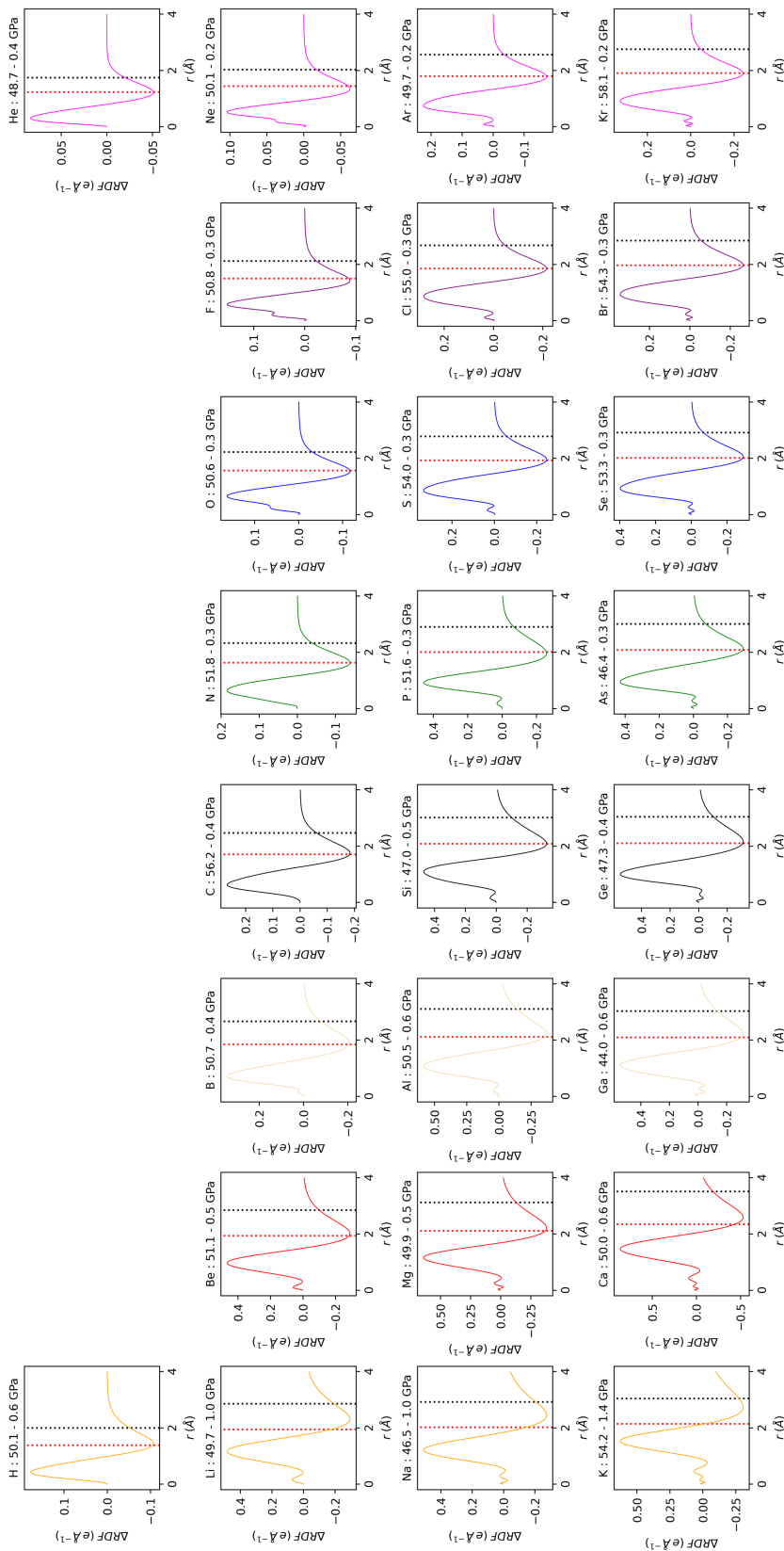


Figure S11: Difference in the radial distribution function of atoms at  $\sim 50$  and  $\sim 1$  GPa for the main group elements from hydrogen to krypton.