

# CCSD(T) calculations of confined systems: In crystal polarizabilities of anions.

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We present isotropic dipole polarizabilities of a series of the  $F^-$ ,  $Cl^-$ ,  $O^{2-}$ , and  $S^{2-}$  anions in LiF, LiCl, NaF, NaCl, KF, KCl, ZnO, ZnS, MgO, MgS, CaO, CaS, SrO, SrS, BaO, BaS and other crystals containing halogen, oxygen, or sulphur anions. The second electron in free  $O^{2-}$  and  $S^{2-}$  anions is unbound. Both are energetically stabilized in the crystal environment with respect to the singly charged anion and the neutral oxygen or sulphur atoms, respectively. Similarly,  $O^{2-}$  and  $S^{2-}$  anions are substantially stabilized when exposed to an external harmonic-oscillator confining potential. With relatively weak confining potential both  $O^{2-}$  and  $S^{2-}$  anions represent true energy minima and all HF instabilities and the implied broken symmetry solutions disappear [1]. At the same time, polarizabilities of  $F^-$ ,  $Cl^-$ ,  $O^{2-}$ , and  $S^{2-}$  anions confined by an external harmonic-oscillator potential calculated by the CCSD(T) method are considerably reduced in comparison with polarizabilities of free anions. We relate the harmonic-oscillator confining potential  $\omega$  to the experimental anionic polarizabilities which are known for selected crystals. We were able to find anionic polarizabilities resulting from CCSD(T) calculations with a specific confining potential  $\omega$  which are the same as experimental in-crystal polarizabilities. We use these polarizabilities (our training set) as tuning quantities for predicting in-crystal polarizabilities of anions. We observe that so determined values of  $\omega$  depend linearly on the ionic radius of the cation participating in specific crystals containing  $F^-$ ,  $Cl^-$ ,  $O^{2-}$ , or  $S^{2-}$  anions. For predicting in-crystal anionic polarizability for a crystal we only need the ionic radius of the participating cation and the CCSD(T) polarizability of an anion exposed to an external harmonic-oscillator confining potential with a specific  $\omega$  as obtained from the relation between  $\omega$  and the ionic radius of a cation in the training set. We predict in-crystal polarizabilities of  $F^-$ ,  $Cl^-$ ,  $O^{2-}$ , and  $S^{2-}$  anions in a series of crystals having similar structural features as crystals used as a training set.

[1] Holka, F., Neogrady, P., Urban, M., Paldus J., *Coll. Czech. Chem. Commun.* 72: 197-222, 2007.