Week 7: Hartree-Fock and DFT

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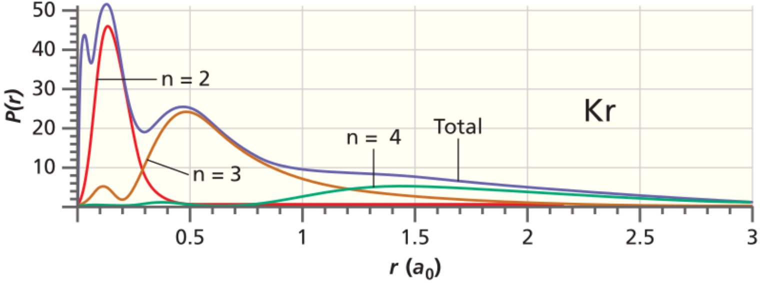
Mini-innføring i PySCF

- … se JupyterHub

Diskusjonsoppgaver



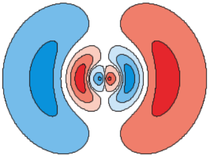
- Q10.2 There are more electrons in the n = 4 shell than for the n = 3 shell in Krypton. However, the peak in the radial distribution in Figure 10.6 is smaller for the n = 4 shell than for the n = 3 shell. Explain this fact.

Flere diskusjonsoppgaver

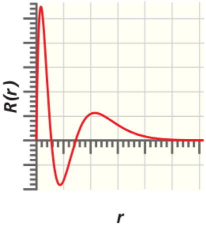
- The effective nuclear charge experienced by a 2s electron in Li is 1.28. We might expect this number to be 1.0 rather than 1.28. Why is ζ larger than 1? Similarly, explain the effective nuclear charge seen by a 2s electron in carbon - what value would you expect?
- Q10.3 How is the effective nuclear charge related to the size of the basis set in a Hartree–Fock calculation?
- Will adding further basis functions to a Hartree-Fock calculation always lead to a decreased energy?
- Q10.17 Is there a physical reality associated with the individual entries of a Slater determinant?
- Why is Hartree-Fock theory only an approximation?
- Both Hartree-Fock theory and Kohn-Sham DFT use Slater determinants. What is the fundamental difference here?
- What are the advantages and drawbacks of DFT? What is the exchange-correlation functional?

Enda flere diskusjonsoppgaver

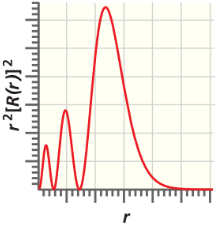
Q10.15 See Question Q10.4 for background information and an explanation of (a), (b), and (c) in the following figures. Identify the orbital.



(a)



(b)



(c)

Regneoppgaver gjort av meg

- P10.5 The operator for the square of the total spin of two electrons is

  $$\hat{S}^2_{\text{total}} = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}).$$

  Given that

  $$\hat{S}_x\alpha = \frac{\hbar}{2}\beta, \quad \hat{S}_y\alpha = \frac{i\hbar}{2}\beta, \quad \hat{S}_z\alpha = \frac{\hbar}{2}\alpha,$$

  and

  $$\hat{S}_x\beta = \frac{\hbar}{2}\alpha, \quad \hat{S}_y\beta = -\frac{i\hbar}{2}\alpha, \quad \hat{S}_z\beta = -\frac{\hbar}{2}\beta,$$

  show that $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are eigenfunctions of the operator $\hat{S}^2_{\text{total}}$. What is the eigenvalue in each case?
- P10.8 (variant) Write a possible Slater determinant for the ground state configuration of Li.

Regneoppgaver

- Oppgave P10.10 i boka
- P10.6 Show that the functions

$$\frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}}$$

and

$$\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$$

are eigenfunctions of
$\hat{S}^2_{\text{total}} = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z})$.
What is the eigenvalue in each case?