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Theoretical Chemistry – Quantum Mechanics II

Problem Set No. 1, 20.04.2015

The problem sets can be downloaded from
`http://www.uni-ulm.de/theochem/`
The problem set will be discussed in the tutorial on 04.05.2014 in N25/2103

Problem 1: Spin-Projection-Operators
Consider two particles with spin $\mathbf{s_1}$ and $\mathbf{s_2}$ ($s_1 = s_2 = \frac{1}{2}$).

a) What is the effect of the operators $P_0 = \frac{1}{4}\hbar^2 - \mathbf{s_1 s_2}$ respectively $P_1 = \frac{3}{4}\hbar^2 + \mathbf{s_1 s_2}$ on an arbitrary state $\chi(s_1, s_2)$?

b) Show that $P_{12}\chi(s_1, s_2) = \chi(s_2, s_1)$, where P_{12} is given by $P_{12} = \frac{1}{2}\hbar^2 + 2\mathbf{s_1 s_2}$.

Hint: Express $\mathbf{S_1} \cdot \mathbf{S_2}$ through $S^2 = (\mathbf{S_1} + \mathbf{S_2})^2$ and use the singlet-triplet representation of the spin wave function. Note that $\mathbf{S_i}^2 = 3/4$ (Why?).

Aufgabe 2: Two-electrons-atom in perturbation theory
In 1-st order perturbation theory, the contribution of the electron-electron interaction in the two-electrons-atom is given by (cp. eq. 6.29)

$$\Delta^{(1)}_{1s^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle_{1s^2} = \int\int \frac{Z^6}{\pi^2 a_0^6} e^{-2Z(r_1+r_2)/a_0} \frac{e^2}{r_{12}} \, d^3r_1 \, d^3r_2 \tag{1}$$

In contrast to the lecture, use the Fourier representation of $1/|\mathbf{r}_1 - \mathbf{r}_2| = 1/r_{12}$

$$\frac{1}{r_{12}} = \int \frac{d^3k}{(2\pi)^3} \exp(i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)) \frac{4\pi}{k^2} \ , \tag{2}$$

to calculate the perturbation term. Through this replacement the integrals over d^3r_1 and d^3r_2 will be de-coupled.

Hint: Use without any proof the following integrals:

$$\int d^3r \exp(-\alpha r) \exp(i\mathbf{k} \cdot \mathbf{r}) \ = \frac{8\pi\alpha}{(k^2 + \alpha^2)^2} \ , \tag{3}$$

$$\int_0^\infty \frac{dx}{(1 + x^2)^4} = \frac{5\pi}{32} \ . \tag{4}$$