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Problem Sheet 11
for the tutorial on July 18th, 2025
Quantum Mechanics II
Summer term 2025

Sheet handed out on July 8th, 2025; to be handed in on July 15th, 2025 until 2 pm

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Exercise 11.1: Spin [7+5 P.]

a) Consider two spin-1/2 particles. Show explicitly that the total spin is $S = 0$ for the singlet-state

$$|\chi_1\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \tag{1}$$

and $S = 1$ for each of the following triplet states

$$\begin{aligned} |\chi_2\rangle &= |\uparrow\uparrow\rangle \ , \\ |\chi_3\rangle &= \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \ , \\ |\chi_4\rangle &= |\downarrow\downarrow\rangle \ . \end{aligned} \tag{2}$$

b) Show that

$$\hat{P}_1 = \frac{3}{4} + \frac{1}{\hbar^2} \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 \tag{3}$$

projects onto the triplet subspace.

Exercise 11.2: Perturbative approach for Helium's first autoionizing state [13 P.]

Let us consider the Auger decay of the autoionizing state $2s^2$ of Helium. Hereby one electron is emitted in the continuum while simultaneously the second one decays to the $1s$ ground state of the resulting He^+ ion. Using energy conservation arguments, find the continuum electron energy in eV. You may use the Schrödinger energy solution known for the H-like helium ion and apply first order perturbation theory like in the lecture to determine the energy of the autoionizing state. Thereby you may employ the non-relativistic radial wave functions for the 2s electrons given by

$$\Psi_{200}(r) = \sqrt{\frac{Z^3}{32\pi a_0^3}} \left(-\frac{Zr}{a_0} + 2\right) \mathrm{e}^{-Zr/(2a_0)} \ . \tag{4}$$

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b) Show that

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projects onto the triplet subspace.

$$J^2 = (\vec{J}_1 + \vec{J}_2)^2 = J_1^2 + J_2^2 + 2\vec{J}_1 \cdot \vec{J}_2$$

$$= J_1^2 + J_2^2 + 2J_{1z}J_{2z} + J_{1+}J_{2-} + J_{1-}J_{2+}$$

χ_1: $\sigma_{1x}\sigma_{2x}|\chi_1\rangle = \frac{1}{\sqrt{2}}\left(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle\right) = -|\chi_1\rangle$

$\sigma_{1y}\sigma_{2y}|\chi_1\rangle = -|\chi_1\rangle$ similarly

$\sigma_{1z}\sigma_{2z}|\chi_1\rangle = -|\chi_1\rangle$ because spins are opposite

since $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$,

$$\vec{S}_1 \cdot \vec{S}_2 |\chi_1\rangle = (-3)\frac{\hbar^2}{4}|\chi_1\rangle = -\frac{3\hbar^2}{4}|\chi_1\rangle$$

$$S_1^2|\chi_1\rangle = \hbar^2\left(\tfrac{1}{2}\right)\left(\tfrac{1}{2}+1\right) = \frac{3\hbar^2}{4}$$

$$\left(S_1^2 + S_2^2 + 2\vec{S}_1\cdot\vec{S}_2\right)|\chi_1\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2\left(\frac{3\hbar^2}{4}\right)\right)|\chi_1\rangle = 0$$

0 eigenvalue

χ_2: $\left(S_1^2 + S_2^2 + 2S_{1z}S_{2z} + S_{1+}S_{2-} + S_{1-}S_{2+}\right)|\uparrow\uparrow\rangle$

kill the stuff

$$= \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\frac{\hbar^2}{4}\right)|\uparrow\uparrow\rangle = 2\hbar^2|\uparrow\uparrow\rangle$$

$$= \hbar^2(1)(1+1)|\uparrow\uparrow\rangle$$

$\Rightarrow S = 1$

χ_3:

$$\sigma_{x_1}\sigma_{x_2}\left[\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right] = |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$$

$$\sigma_{y_1}\sigma_{y_2}\left[\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right] = |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \quad \text{(there's one } i(-i) \text{ in there)}$$

$$\sigma_{z_1}\sigma_{z_2}\left[\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right] = -\left[\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right]$$

$$\left(S_1^2 + S_2^2 + 2\vec{S}_1\cdot\vec{S}_2\right)|\chi_3\rangle = \left[\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\left(\frac{\hbar^2}{4}\right)\right]|\chi_3\rangle$$

$$= 2\hbar^2|\chi_3\rangle$$

Hence $s = 1$

χ_4: Exactly the same calculation as for χ_2.

b) Show that

$$\hat{P}_1 = \frac{3}{4} + \frac{1}{\hbar^2}\hat{S}_1\cdot\hat{S}_2 \tag{3}$$

projects onto the triplet subspace.

By reading off from above, we see that

$$\hat{P}_1 = \frac{3}{4} + \frac{1}{2\hbar^2}\left(S^2 - \underbrace{S_1^2 - S_2^2}_{\text{always } \frac{3\hbar^2}{4}}\right)$$

$$= \frac{3}{4} + \frac{1}{2\hbar^2}\left(S^2 - \frac{3}{2}\hbar^2\right)$$

$$= \frac{1}{2\hbar^2}S^2$$

$$P_1|\chi_i\rangle = \begin{cases} 0 & i = 1 \\ \underbrace{\frac{1}{2\hbar^2}(2\hbar^2)}_{1} & \text{else.} \end{cases}$$

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Hydrogen atom: $E_n = -\frac{me^4}{2\hbar^2 n^2}$

Energy of $2s^2$ state: $2\times E_2$ + interaction energy

$$\Delta E = \langle \psi | \frac{e^2}{4\pi\varepsilon_0 r_{12}} | \psi \rangle$$

$$= \frac{e^2}{4\pi\varepsilon_0} \iint \psi^*_{200}(r_1)\psi^*_{200}(r_2) \frac{1}{|r_1 - r_2|} \psi_{200}(r_1)\psi_{200}(r_2)\, d^3r_1\, d^3r_2$$ (spin part falls out as it is normalised)

solid angle

$$= \frac{e^2}{4\pi\varepsilon_0} \int_0^\infty\!\!\int_0^\infty r_1^2 r_2^2\, \psi^*_{200}(r_1)\psi^*_{200}(r_2) \frac{1}{r_1 - r_2} \psi_{200}(r_1)\psi_{200}(r_2)\, dr_1\, dr_2\, d\Omega_1\, d\Omega_2$$

$$= \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z^3}{32\pi a_0^3}\right)^2 \int_0^\infty\!\!\int_0^\infty r_1^2 r_2^2 \left(-\frac{Zr_1}{a_0}+2\right)^2 \left(-\frac{Zr_2}{a_0}+2\right)^2 \frac{1}{|r_1 - r_2|} e^{-\frac{Zr_1}{a_0}} e^{-\frac{Zr_2}{a_0}}\, dr_1\, dr_2\, d\Omega_1\, d\Omega_2$$

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y^*_{lm}(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

$r_>$: bigger r

$$= \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z^3}{32\pi a_0^3}\right)^2 \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \int_0^\infty\!\!\int_0^\infty r_1^2 r_2^2 \frac{r_<^l}{r_>^{l+1}} Y^*_{lm}(\theta_1,\varphi_1) Y_{lm}(\theta_2,\varphi_2) \left(-\frac{Zr_1}{a_0}+2\right)^2$$

$$\left(-\frac{Zr_2}{a_0}+2\right)^2 \exp\left[-\frac{Z(r_1+r_2)}{a_0}\right] dr_1\, dr_2\, d\Omega_1\, d\Omega_2$$

All terms except $l=0$ and $m=0$ vanish by integration

$$= \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z^3}{32\pi a_0^3}\right)^2 (4\pi)^2 \int_0^\infty\!\!\int_0^\infty r_1^2 r_2^2 \frac{1}{r_>} \left(-\frac{Zr_1}{a_0}+2\right)^2 \left(-\frac{Zr_2}{a_0}+2\right)^2 \exp\left[-\frac{Z(r_1+r_2)}{a_0}\right]$$

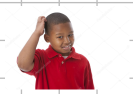
$$= \frac{4\pi e^2}{\varepsilon_0} \left(\frac{Z^3}{32\pi a_0^3}\right)^2 \int_0^\infty r_2^2 \left(-\frac{Zr_2}{a_0}+2\right)^2 e^{-\frac{Zr_2}{a_0}} \left[\int_0^{r_2} r_1^2 \frac{1}{r_2} \left(-\frac{Zr_1}{a_0}+2\right)^2 e^{-\frac{Zr_1}{a_0}} dr_1 \right.$$

$$\left. + \int_{r_2}^\infty r_1^{\cancel{2}} \frac{1}{\cancel{r_1}} \left(-\frac{Zr_1}{a_0}+2\right)^2 e^{-\frac{Zr_1}{a_0}} dr_1 \right] dr_2$$

$$= \frac{4\pi e^2}{\varepsilon_0}\left(\frac{Z^3}{32\pi a_0^3}\right)^2 \int_0^\infty r_2^2\left(-\frac{Zr_2}{a_0}+2\right)^2 e^{-\frac{Zr_2}{a_0}}\left[\frac{8a_0^4 - e^{-\frac{r_2 Z}{a_0}}\left(4a_0^2r_2^2Z^2+8a_0^3r_2Z+8a_0^4+r_2^4Z^4\right)}{r_2a_0Z^3}\right.$$

$$\left. + \frac{e^{-\frac{r_2Z}{a_0}}\left(-a_0r_2^2Z^2+2a_0^2r_2Z+2a_0^3+r_2^3Z^3\right)}{a_0Z^2}\right] dr_2$$

$$= \frac{4\pi e^2}{\varepsilon_0}\left(\frac{Z^3}{32\pi a_0^3}\right)^2 \int_0^\infty r_2^2\left(-\frac{Zr_2}{a_0}+2\right)^2 e^{-\frac{Zr_2}{a_0}}\left[\frac{e^{-\frac{r_2Z}{a_0}}\left(-2a_0r_2^2Z^2+8a_0^3e^{\frac{r_2Z}{a_0}}-6a_0^2r_2Z-8a_0^3-r_2^3Z^3\right)}{r_2Z^3}\right] dr_2$$



This is wrong isn't it, surely it isn't meant to be this hard

$$= \frac{4\pi e^2}{\varepsilon_0}\left(\frac{Z^3}{32\pi a_0^3}\right)^2\left(\frac{77}{8}\frac{a_0^5}{Z^5}\right) = \frac{77}{8}\frac{4\pi e^2}{\varepsilon_0}\frac{Z}{(32\pi)^2 a_0}$$

Energy of $2s^2$ state $= 2\left(-\frac{2me^4}{2\hbar^2(4)}\right) + \frac{77}{8}\frac{4\pi e^2}{\varepsilon_0}\frac{Z}{(32\pi)^2 a_0}$

Energy of $1s^1$ state $= -\frac{2me^4}{2\hbar^2}$

By conservation of energy,

energy of free electron = energy of $1s^1$ state − energy of $2s^2$ state

$$= -\frac{me^4}{\hbar^2} + \frac{me^4}{2\hbar^2} + \frac{77}{8}\frac{4\pi e^2}{\varepsilon_0}\frac{Z}{(32\pi)^2 a_0}$$

$\left(a_0 = \frac{\hbar}{mc\alpha}\right.$

$$= -\frac{me^4}{2\hbar^2} + \frac{77}{8}\frac{4\pi e^2}{\varepsilon_0}\frac{Z}{(32\pi)^2 a_0}$$

$\approx 8.20\,eV$