Quantentheorie II Übung 6

Besprechung: 2021WE22 (KW22)

SS 2021 Prof. Dominik Stöckinger (IKTP)

1. **Questions**

   (a) Which of the following operators are possible in a system of two identical particles?

   $$\vec{x}_1 - \vec{x}_2\,, \quad \vec{x}_1 + \vec{x}_2\,, \quad (\vec{x}_1 - \vec{x}_2)^2\,, \quad \vec{p}_1 \cdot \vec{p}_2$$

   (b) Repeat the 1-dimensional potential well problem. What are the energy eigenstates and eigenvalues?

   (c) What is the hydrogen molecule Hamiltonian only with the Coulomb interaction and without spins?

   (d) Which Hamiltonian eigenstates are used to describe the hydrogen molecules in the Heitler-London theory?

2. **Two identical particles in potential well:** two identical particles are in a one-dimensional potential well

   $$V(r) = \begin{cases} 0\,, & \text{for } |r| < r_0\,, \\ \infty\,, & \text{for } |r| \geq r_0\,. \end{cases}$$

   The two particles do not interact with each other and are in parallel spin states: the magnetic quantum numbers of both particles are the same, m_s.

   (a) Write down the Hamiltonian of this two-particle system and show that the energy eigenstates can be factorized into space and spin parts.

   (b) What are the allowed space wave functions for bosons and fermions respectively when we consider the spin state assumption above?

   (c) Write down the energy eigenstates and eigenvalues for bosons and fermions and specify the groundstate energies.

3. **Hydrogen molecule without spin:** the approximate groundstate energy of hydrogen molecules can be calculated using the Rayleigh–Ritz method (Variationsverfahren). We take a trial state $|g\rangle$,

   $$|g\rangle = c_1|\phi_a^{(1)}\rangle|\phi_b^{(2)}\rangle + c_2|\phi_b^{(1)}\rangle|\phi_a^{(2)}\rangle\,,$$

   where c_1 and c_2 are real numbers and should be determined appropriately. $|\phi_{a,b}^{(i)}\rangle$ are the eigenstates of

   $$\left(\frac{\vec{p}_i^2}{2m} - \frac{\alpha}{r_{iA}}\right)|\phi_A^{(i)}\rangle = E_A|\phi_A^{(i)}\rangle\,,$$

   with $A \in \{a, b\}$ and $i \in \{1, 2\}$ as introduced from the lecture.

(a) Write the Hamiltonian of the hydrogen molecule H and compute

$$\langle H \rangle_g = \frac{\langle g|H|g\rangle}{\langle g|g\rangle} \, .$$

(b) What condition should be satisfied if $|g\rangle$ is a groundstate and what is the relation of c_1 and c_2 obtained from the condition?

(c) Write down the symmetric and antisymmetric groundstates $|g\rangle^{(\pm)}$ and the eigenvalues $E_\pm$. Compare the results from the lecture.

4. **Hydrogen molecule with spin:** we now consider the spins of the electrons.

(a) Write down the symmetric (+) and antisymmetric (−) spin states $|S\, m_S\rangle^{(\pm)}$ using the total spin quantum numbers $\vec{S} = \vec{S}_1 + \vec{S}_2$ and $m_S = m_{S_1} + m_{S_2}$.

(b) The space part of the wave function (see lecture or previous exercise) satisfies

$$\frac{{}^{(\pm)}\langle g|H|g\rangle^{(\pm)}}{{}^{(\pm)}\langle g|g\rangle^{(\pm)}} = E_\pm \, .$$

Now we search for an equivalent Hamiltonian $\hat{H}_{\text{spin}}$ which applies only to the spin part, i.e. depends only on the spin operators $\vec{S}_1$ and $\vec{S}_2$. Construct the operator $\hat{H}_{\text{spin}}$ which produces eigenvalues

$$\hat{H}_{\text{spin}}|S\, m_S\rangle^{(\mp)} = E_\pm |S\, m_S\rangle^{(\mp)} \, .$$

(c) Discuss the preferred spin state for the energy groundstate.

1. **Questions**

(a) Which of the following operators are not possible in a system of two identical particles?

$$\underset{A}{\vec{x}_1 - \vec{x}_2}, \quad \underset{B}{\vec{x}_1 + \vec{x}_2}, \quad \underset{C}{(\vec{x}_1 - \vec{x}_2)^2}, \quad \underset{D}{\vec{p}_1 \cdot \vec{p}_2}$$

(b) Repeat the 1-dimensional potential well problem. What are the energy eigenstates and eigenvalues?

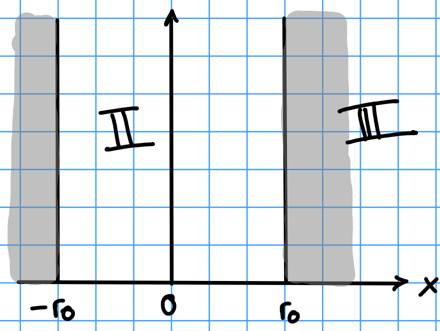
(c) What is the hydrogen molecule Hamiltonian only with the Coulomb interaction and without spins?

(d) Which Hamiltonian eigenstates are used to describe the hydrogen molecules in the Heitler-London theory?

b) $\psi(x) = A\cos kx + B\sin kx$

$\psi_I = \psi_{III} = 0$

$\psi(\pm r_0) = 0$



$A = 0 \quad \sin(k r_0) = 0$ ungerade

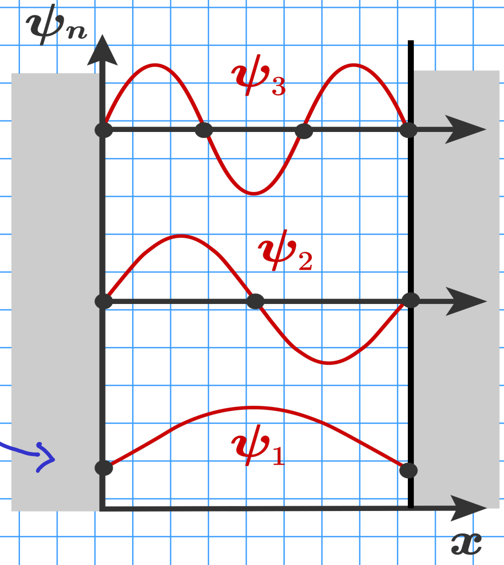
$\Leftrightarrow k r_0 = n\pi$

$B = 0 \quad \cos(k r_0) = 0$ gerade

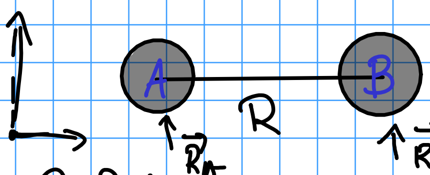
$\Leftrightarrow k r_0 = (2n+1)\frac{\pi}{2}$

Grundzustand

$E = \frac{k^2}{2m}$



c)



$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \alpha\left(\frac{1}{r_{A1}} + \frac{1}{r_{A2}} + \frac{1}{r_{B1}} + \frac{1}{r_{B2}} - \frac{1}{r_{12}} - \frac{1}{R}\right)$$

R = fest. Born Oppenheimer Näherung

d) $|\psi\rangle^{\pm} = \underbrace{|\phi_A \phi_B\rangle^{\pm}} \otimes |S\,M\rangle$

LCAO H_2^+

$\phi_A = \psi_{A,100}$ Grundzustand H-Atom A $\vec{R}_A$

$|\psi\rangle = C_A|\phi_A\rangle + C_B|\phi_B\rangle$

2. **Two identical particles in potential well:** two identical particles are in a one-dimensional potential well

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The two particles do not interact with each other and are in parallel spin states: the magnetic quantum numbers of both particles are the same, m_s.

(a) Write down the Hamiltonian of this two-particle system and show that the energy eigenstates can be factorized into space and spin parts.

(b) What are the allowed space wave functions for bosons and fermions respectively when we consider the spin state assumption above?

(c) Write down the energy eigenstates and eigenvalues for bosons and fermions and specify the groundstate energies.

a) $H = \left(-\frac{1}{2m} \frac{d^2}{dr_2^2} + V(r_2) \right) + \left(-\frac{1}{2m} \frac{d^2}{dr_1^2} + V(r_1) \right)$ nur Ort

$H|\psi\rangle = E|\psi\rangle$

$[H, S^2] = [H, S_z] = 0 \qquad |\psi\rangle = |r\rangle |s\, m_s\rangle$

b) $|r\rangle$ boson : symmetrisch

$|r\rangle$ fermion : antisymmetrisch

$|r\rangle^{\pm} = \frac{1}{\sqrt{2}} \left(|\varphi_n^p(1)\, \varphi_{n'}^{p'}(2)\rangle \pm |\varphi_n^p(2)\, \varphi_{n'}^{p'}(1)\rangle \right)$

c) Grundzustand

Boson $\quad n = 0 = n' \quad p = p' = + \qquad E_0^B = 2E_0^{(+)} = \frac{\pi^2}{4mr_0^2}$

Fermion $\quad n = 0,\ n' = 1 \quad p = +,\ p' = - \qquad E_0^F = E_0^+ + E_1^- = \frac{5}{8} \frac{\pi^2}{mr_0^2}$

$E_n^{(+)} = \frac{\pi^2}{2mr_0^2} \left(n + \frac{1}{2} \right)^2 \qquad n = 0, \ldots$

$E_n^{(-)} = \frac{\pi^2}{2mr_0^2} n^2 \qquad n = 1, \ldots$

3. **Hydrogen molecule without spin:** the approximate groundstate energy of hydrogen molecules can be calculated using the Rayleigh–Ritz method (Variationsverfahren). We take a trial state $|g\rangle$,

$$|g\rangle = c_1|\phi_a^{(1)}\rangle|\phi_b^{(2)}\rangle + c_2|\phi_b^{(1)}\rangle|\phi_a^{(2)}\rangle,$$

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|\phi_A^1\phi_B^2\rangle \pm |\phi_A^2\phi_B^1\rangle\right)$$

where c_1 and c_2 are real numbers and should be determined appropriately. $|\phi_{a,b}^{(i)}\rangle$ are the eigenstates of

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a)

$$\langle g|H|g\rangle = \overbrace{(c_1^2+c_2^2)}^{1}\,(\overbrace{E_a+E_b}^{2E_1} + C_{AB}) + 2c_1c_2\,(E_a+E_b)\,\overbrace{|L_{AB}|^2}^{1}$$
$$+\,2c_1c_2\,A_{AB}$$

$$\langle g|g\rangle = (c_1^2+c_2^2)\cdot 1 + 2c_1c_2\,|L_{AB}|^2$$

$$L_{AB} = \langle\phi_A|\phi_B\rangle$$

$$A_{AB} = \langle\phi_A^{(1)}|-\frac{\alpha}{r_{1b}}|\phi_B^{(1)}\rangle L_{AB}^* + \ldots \quad -\frac{\alpha}{r_{2A}}$$

$$+\,\langle\phi_A^1\phi_B^2|\frac{1}{r_{12}}|\phi_B^1\phi_A^2\rangle + \frac{\alpha}{R}|L_{AB}|^2$$

$$\langle H\rangle_g = E_a+E_b + \frac{(c_1^2+c_2^2)\,C_{AB} + 2c_1c_2A_{AB}}{c_1^2+c_2^2+2c_1c_2|L_{AB}|^2}$$

b) VL $c_1 = \mp c_2 = \frac{1}{\sqrt{2}}$ $\quad c_1^2+c_2^2 = 1$ (Normierung)

$$\frac{\partial\langle H\rangle_g}{\partial c_1} = 0 \qquad \frac{\partial\langle H\rangle_g}{\partial c_2} = 0 \qquad \Rightarrow c_1^2 = c_2^2$$

$$\Rightarrow c_1 = \pm c_2$$

$$\frac{\partial\langle H\rangle_g}{\partial c_1} = \frac{2c_2\,(C_{AB}\,|L_{AB}|^2 - A_{AB})\,\overbrace{(c_1^2-c_2^2)}}{(c_1^2+c_2^2+2c_1c_2|L_{AB}|^2)^2}$$

c) $\Rightarrow \quad |g\rangle = |\phi_A^1 \phi_B^2\rangle \pm |\phi_B^1 \phi_A^2\rangle$

$$E^{\pm} = E_a + E_b + \frac{C_{AB} \pm A_{AB}}{1 \pm |L_{AB}|^2}$$

HL Näherung

$|L_{AB}|^2 \approx 0$

$$\hat{=} \quad E_a + E_b + C_{AB} \pm A_{AB}$$

$A_{AB} < 0 \qquad \Rightarrow \underset{\text{symm.}}{E^+} < \underset{\text{antisymm.}}{E^-}$

Grundzustand $\quad \Rightarrow$ Spin antisym.

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(c) Discuss the preferred spin state for the energy groundstate.

a) zwei Teilchen 1, 2 $\quad |S_1\, S_2\, m_{S_1}\, m_{S_2}\rangle$

$\rightarrow |S, m_S\rangle$

Singlet (antisymm.) $\quad |S, m_S\rangle^S = |0,0\rangle \longrightarrow \dfrac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$

Triplet (symm.) $\quad |S, m_S\rangle^T = \begin{cases} |1,+1\rangle \\ |1,0\rangle \\ |1,-1\rangle \end{cases}$

$S^2|s,m\rangle = (s+1)s|s,m\rangle$

$S_1|s\, m\rangle = s_1(s_1+1)|s, m\rangle$

b) $S^2 = (S_1+S_2)^2 = S_1^2 + S_2^2 + 2S_1\cdot S_2$

$S_1\cdot S_2 = \frac{1}{2}(S^2 - S_1^2 - S_2^2)$

$S_1\cdot S_2|0,0\rangle = \frac{1}{2}\left(0 - \frac{3}{4} - \frac{3}{4}\right)|0,0\rangle = -\frac{3}{4}|0,0\rangle$

$S_1\cdot S_2|1\, m_S\rangle = \frac{1}{2}\left(2 - \frac{3}{4} - \frac{3}{4}\right)|1\, m_S\rangle = \frac{1}{4}|1\, m_S\rangle$

$H_{spin} = \hat{\vec{S}}_1\cdot\hat{\vec{S}}_2 \cdot \beta + \alpha \mathbb{1}$

$H_{spin}|0,0\rangle = \left(\alpha - \frac{3}{4}\beta\right)|00\rangle = E_+|00\rangle$

$H_{spin}|1\, m_S\rangle = \left(\alpha + \frac{1}{4}\beta\right)|1\, m_S\rangle = E_-|00\rangle$

$\alpha = \dfrac{E_+ + 3E_-}{4} \qquad \beta = E_- - E_+$

$$\hat{H}_{spin} = \frac{E_+ + 3E_-}{4} + \underbrace{(E_- - E_+)}_{\text{positiv}} \underbrace{\hat{S}_1 \cdot \hat{S}_2}$$

$\longrightarrow$ sollte negativ sein

c) 3. $\Rightarrow$ Grundzustand symmetrisch $E_+ < E_-$ $E \rightarrow min$

$\Rightarrow$ Spin sollte $|00\rangle$ sein $\Rightarrow$ antisymm.