Quantentheorie II Übung 6

– Sample solutions –

SS 2021 Dr. H. Stöckinger-Kim, Prof. Dominik Stöckinger (IKTP)

2. **Two identical particles in potential well:** the eigenstates of the potential are

- + parity eigenstates and eigenvalues:

$$\phi_n^+(r) = \frac{1}{\sqrt{r_0}} \cos(\frac{\pi}{2r_0}(2n+1)r), \tag{1}$$

$$E_n^+ = \frac{\pi^2}{2mr_0^2}(n+\frac{1}{2})^2, \text{ where } n = 0, 1, 2, \cdots . \tag{2}$$

- − parity eigenstates and eigenvalues:

$$\phi_n^-(r) = \frac{1}{\sqrt{r_0}} \sin(\frac{\pi}{r_0}nr), \tag{3}$$

$$E_n^- = \frac{\pi^2}{2mr_0^2}n^2, \text{ where } n = 1, 2, 3, \cdots . \tag{4}$$

(a) As the two particle do not interact with each other, the Hamiltonian of this system is the sum of the Hamiltonian of each particle

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \left(-\frac{1}{2m}\frac{d^2}{dr_1^2} + V(r_1)\right) + \left(-\frac{1}{2m}\frac{d^2}{dr_2^2} + V(r_2)\right). \tag{5}$$

$\hat{H}$ contains no spin part and commutes with total spin operators S^2, and S_z: $[H, S^2] = [H, S_z] = 0$. Therefore simultaneous eigenstates exist $|\psi\rangle = |r\rangle|S, m_s\rangle^+$, where $|r\rangle$ is an eigenstate of $\hat{H}$, and the spin state is assumed to be parallel (symmetric). For bosons $|r\rangle$ should be symmetric, and for fermions anti-symmetric.

(b) The space wave function is $\langle x|\Phi_{n,n'}^{p,p'}\rangle^{\pm} = \frac{1}{\sqrt{2}}(\phi_n^p(r_1)\phi_{n'}^{p'}(r_2) \pm \phi_n^p(r_2)\phi_{n'}^{p'}(r_1))$ (+ for bosons and − for fermions), where ϕ_n^p are in Eqs. (1) and (3).

(c) Energy eigenstates and eigenvalues for bosons:
$|\Phi_{n,n'}^{p,p'}\rangle^+|S, m_s\rangle^+$, $E_{n,n'}^{p,p'} = E_n^p + E_{n'}^{p'}$.
Energy eigenstates and eigenvalues for fermions:
$|\Phi_{n,n'}^{p,p'}\rangle^-|S, m_s\rangle^+$, $E_{n,n'}^{p,p'} = E_n^p + E_{n'}^{p'}$, $(n,p) \neq (n',p')$.
Groundstate energy:
bosons: $n = n' = 0$, $p = p' = +$ $\implies$ $E_0^B = 2E_0^+ = \frac{\pi^2}{4mr_0^2}$.
fermions: $n = 0, p = +$ and $n' = 1, p = -$ $\implies$ $E_o^F = E_0^+ + E_1^- = \frac{5}{8}\frac{\pi^2}{mr_0^2}$

3. **Hydrogen molecule without spin:**

(a) The Hamiltonian is

$$\hat{H} = \sum_{i=1}^{2}\left(\frac{p_i^2}{2m} - \frac{\alpha}{r_{ia}} - \frac{\alpha}{r_{ib}}\right) + \frac{\alpha}{r_{12}} + \frac{\alpha}{R_{ab}}. \tag{6}$$

For the trial state $|g\rangle$ we obtain

$$\langle g|\hat{H}|g\rangle = (c_1^2 + c_2^2)\langle\phi_a^{(1)}\phi_b^{(2)}|\hat{H}|\phi_a^{(1)}\phi_b^{(2)}\rangle + 2c_1c_2\,\mathrm{Re}(\langle\phi_a^{(1)}\phi_b^{(2)}|\hat{H}|\phi_b^{(1)}\phi_a^{(2)}\rangle), \tag{7}$$

$$\Longleftarrow\ \langle\phi_a^{(1)}\phi_b^{(2)}|\hat{H}|\phi_b^{(1)}\phi_a^{(2)}\rangle = \langle\phi_b^{(1)}\phi_a^{(2)}|\hat{H}|\phi_a^{(1)}\phi_b^{(2)}\rangle^* \tag{8}$$

and

$$\begin{aligned}
&\langle\phi_a^{(1)}\phi_b^{(2)}|\hat{H}|\phi_a^{(1)}\phi_b^{(2)}\rangle \\
&= \langle\phi_a^{(1)}|\frac{p_1^2}{2m} - \frac{\alpha}{r_{1a}}|\phi_a^{(1)}\rangle + \langle\phi_b^{(2)}|\frac{p_2^2}{2m} - \frac{\alpha}{r_{2b}}|\phi_b^{(2)}\rangle \Longleftarrow \langle\phi_A^{(i)}|\phi_A^{(i)}\rangle = 1 \\
&+ \langle\phi_a^{(1)}|\frac{-\alpha}{r_{1b}}|\phi_a^{(1)}\rangle + \langle\phi_b^{(2)}|\frac{-\alpha}{r_{2a}}|\phi_b^{(2)}\rangle + \langle\phi_a^{(1)}\phi_b^{(2)}|\frac{\alpha}{r_{12}}|\phi_a^{(1)}\phi_b^{(2)}\rangle + \langle\phi_a^{(1)}\phi_b^{(2)}|\frac{\alpha}{R_{ab}}|\phi_a^{(1)}\phi_b^{(2)}\rangle \\
&= E_a + E_b + C_{ab} = \langle\phi_b^{(1)}\phi_a^{(2)}|\hat{H}|\phi_b^{(1)}\phi_a^{(2)}\rangle,
\end{aligned} \tag{9}$$

where

$$C_{ab} \equiv \langle\phi_a^{(1)}|\frac{-\alpha}{r_{1b}}|\phi_a^{(1)}\rangle + \langle\phi_b^{(2)}|\frac{-\alpha}{r_{2a}}|\phi_b^{(2)}\rangle + \langle\phi_a^{(1)}\phi_b^{(2)}|\frac{\alpha}{r_{12}}|\phi_a^{(1)}\phi_b^{(2)}\rangle + \langle\phi_a^{(1)}\phi_b^{(2)}|\frac{\alpha}{R_{ab}}|\phi_a^{(1)}\phi_b^{(2)}\rangle. \tag{10}$$

Also

$$\mathrm{Re}(\langle\phi_a^{(1)}\phi_b^{(2)}|\hat{H}|\phi_b^{(1)}\phi_a^{(2)}\rangle) = E_a|L_{ab}|^2 + E_b|L_{ab}|^2 + A_{ab}, \Longleftarrow \langle\phi_a|\phi_b\rangle = \langle\phi_b|\phi_a\rangle^* \equiv L_{ab} \tag{11}$$

where

$$A_{ab} = \frac{\alpha}{R_{ab}}|L_{ab}|^2 + \mathrm{Re}(\langle\phi_a^{(1)}|\frac{-\alpha}{r_{1b}}|\phi_b^{(1)}\rangle L_{ab}^* + \langle\phi_b^{(2)}|\frac{-\alpha}{r_{2a}}|\phi_a^{(2)}\rangle L_{ab} + \langle\phi_a^{(1)}\phi_b^{(2)}|\frac{\alpha}{r_{12}}|\phi_b^{(2)}\phi_a^{(2)}\rangle). \tag{12}$$

From Eqs. (9) and (11) we obtain

$$\langle g|\hat{H}|g\rangle = (c_1^2 + c_2^2)(E_a + E_b + C_{ab}) + 2c_1c_2(E_a + E_b)|L_{ab}|^2 + 2c_1c_2A_{ab}. \tag{13}$$

Further we obtain

$$\langle g|g\rangle = c_1^2 + c_2^2 + 2c_1c_2|L_{ab}|^2. \tag{14}$$

After combining all together we obtain

$$\begin{aligned}
\langle\hat{H}\rangle_g &= \frac{\langle g|\hat{H}|g\rangle}{\langle g|g\rangle} \\
&= E_a + E_b + \frac{(c_1^2 + c_2^2)C_{ab} + 2c_1c_2A_{ab}}{c_1^2 + c_2^2 + 2c_1c_2|L_{ab}|^2}.
\end{aligned} \tag{15}$$

(b) c_1 and c_2 are variables. If $|g\rangle$ is the groundstate, $\frac{\partial \langle H \rangle_g}{\partial c_1} = 0$ (equivalently $\frac{\partial \langle H \rangle_g}{\partial c_2} = 0$),

$$\frac{\partial \langle H \rangle_g}{\partial c_1} = \frac{2c_2(C_{ab}|L_{ab}|^2 - A_{ab})(c_1^2 - c_2^2)}{c_1^2 + c_2^2 + 2c_1c_2|L_{ab}|^2}, \tag{16}$$

and non-zero solutions are $c_1 = \pm c_2$.

(c) The eigenstates with $c_1 = \pm c_2$ are

$$|g\rangle^{\pm} = |\phi_a^{(1)}\phi_b^{(2)}\rangle \pm |\phi_b^{(1)}\phi_a^{(2)}\rangle, \tag{17}$$

which are the symmetric (+) and anti-symmetric (−) states from the lecture. The corresponding energies are

$$\begin{aligned} E^{\pm} = \langle \hat{H} \rangle_g^{\pm} &= E_a + E_b + \frac{C_{ab} \pm A_{ab}}{1 \pm |L_{ab}|^2} \\ &\approx E_a + E_b + C_{ab} \pm A_{ab} \mp C_{ab}|L_{ab}|^2 - A_{ab}|L_{ab}|^2, \end{aligned} \tag{18}$$

and for sufficiently large distance, $|L_{ab}| \ll 1$,

$$E^{\pm} \approx E_a + E_b + C_{ab} \pm A_{ab}. \tag{19}$$

As $A_{ab} < 0$, $E^+ < E^-$, which means that the symmetric state $|g\rangle^+$ energy is lower than the anti-symmetric one.

4. **Hydrogen molecule with spin:**

(a) We set $\vec{S}_1$ for particle 1 and $\vec{S}_2$ for particle 2 and the total spin state is expressed as $|S_1, S_2; m_{S_1}, m_{S_2}\rangle$, which can be expressed in terms of the total spin $\vec{S} = \vec{S}_1 + \vec{S}_2$ as $|S_1, S_2; S, m_S\rangle$ or simply $|S, m_S\rangle$. The singlet state is $|S, m_S\rangle^{\mathrm{S}} = |0, 0\rangle$ and the the triplet states are $|S, m_S\rangle^{\mathrm{T}} \in \{|1, 1\rangle, |1, 0\rangle, |1, -1\rangle\}$. Each triplet state is the eigenstate of S^2, where $S^2 = (\vec{S}_1 + \vec{S}_2)^2 = S_1^2 + S_2^2 + 2\vec{S}_1 \cdot \vec{S}_2$, from which we obtain $\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2}(S^2 - S_1^2 - S_2^2)$. $\vec{S}_1 \cdot \vec{S}_1$ is independent of m_S and explicitly

$$\vec{S}_1 \cdot \vec{S}_2 |0, 0\rangle = -\frac{3}{4}|0, 0\rangle, \tag{20}$$

$$\vec{S}_1 \cdot \vec{S}_2 |1, m_S\rangle = \frac{1}{4}|1, m_S\rangle. \tag{21}$$

$\hat{H}_{\mathrm{spin}}$ applies only to the spin part and we set $\hat{H}_{\mathrm{spin}}^{\mp} = E_{\pm}|S, m_S\rangle^{\mp}$.
Let $\hat{H}_{\mathrm{spin}} = \alpha + \beta \vec{S}_1 \cdot \vec{S}_2$ and we obtain the following equations

$$\hat{H}_{\mathrm{spin}}|0, 0\rangle = (\alpha - \frac{3}{4})|0, 0\rangle = E^+|0, 0\rangle, \tag{22}$$

$$\hat{H}_{\mathrm{spin}}|1, m_S\rangle = (\alpha + \frac{1}{4})|1, m_S\rangle = E^-|1, m_S\rangle, \tag{23}$$

from which we obtain

$$\hat{H}_{\mathrm{spin}} = \frac{E^+ + 3E^-}{4} + (E^- - E^+)\vec{S}_1 \cdot \vec{S}_2. \tag{24}$$

(b) As $E^+ < E^-$ (see the task 3-c), the space wave function part is symmetric for the groundstate. Therefore the preferred spin state is the anti-symmetric spin singlet state.