Solutions to PC3130 AY0708 Paper

1(a) Time-independent Schrodinger equation: $\left[\frac{p^2}{2m}+V(\vec{x})\right]\psi(\vec{x})=E\psi(\vec{x})$

By spherical symmetry, we write $V(\vec{x})=V(r)$, $\psi(\vec{x})=\psi(r,\theta,\phi)=R(r)Y_l^m(\theta,\phi)$

Substitute $p^2=p_r^2+\frac{l^2}{r^2}$ into the Schrodinger equation,

$$\left[\frac{p_r^2}{2m}+\frac{l^2}{2mr^2}+V(r)\right]R(r)Y_l^m(\theta,\phi)=ER(r)Y_l^m(\theta,\phi)$$

Since $p_r=\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r$, $p_r^2=-\hbar^2\frac{1}{r}\frac{\partial}{\partial r}r\frac{1}{r}\frac{\partial}{\partial r}r=-\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r$ and $l^2Y_l^m=\hbar^2 l(l+1)Y_l^m$, we have

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]R(r)Y_l^m(\theta,\phi)=ER(r)Y_l^m(\theta,\phi)$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}+\frac{\hbar^2 l(l+1)}{2mr^2}\frac{1}{r}+V(r)\frac{1}{r}\right]rR(r)=ER(r)$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]rR(r)=ErR(r)$$

Let $y(r)=rR(r)$, we have

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]y(r)=Ey(r)$$

$$\left[\frac{\partial^2}{\partial r^2}-\frac{l(l+1)}{r^2}+\frac{2m}{\hbar^2}(E-V(r))\right]y(r)=0$$

We have reduced the Schrodinger equation to 1D radial equation. (shown)

1(b) $\left[\frac{\partial^2}{\partial\rho^2}-\frac{l(l+1)}{\rho^2}-\frac{1}{4}+\frac{n}{\rho}\right]y(\rho)=0$

Consider boundary conditions at $\rho\to 0$ and $\rho\to\infty$:

When $\rho\to 0$, $\left[\frac{\partial^2}{\partial\rho^2}-\frac{l(l+1)}{\rho^2}\right]y(\rho)=0 \quad\Rightarrow\quad y(\rho)\approx\rho^{l+1}$

When $\rho\to\infty$, $\left[\frac{\partial^2}{\partial\rho^2}-\frac{1}{4}\right]y(\rho)=0 \quad\Rightarrow\quad y(\rho)\approx e^{-\rho/2}$

Let $V(\rho)$ to represent the behaviour of $y(\rho)$ between 0 and ∞,

$$\therefore y(\rho)=\rho^{l+1}V(\rho)e^{-\rho/2} \text{ (shown)}$$

$$y'(\rho)=(l+1)\rho^l V(\rho)e^{-\rho/2}+\rho^{l+1}V'(\rho)e^{-\rho/2}-\frac{1}{2}\rho^{l+1}V(\rho)e^{-\rho/2}$$

$$y''(\rho) = l(l+1)\rho^{l-1}V(\rho)e^{-\rho/2} + (l+1)\rho^l V'(\rho)e^{-\rho/2} - \frac{1}{2}\rho^l V(\rho)e^{-\rho/2} +$$

$$+ (l+1)\rho^l V'(\rho)e^{-\rho/2} + \rho^{l+1}V''(\rho)e^{-\rho/2} - \frac{1}{2}\rho^{l+1}V'(\rho)e^{-\rho/2}$$

$$-\frac{1}{2}(l+1)\rho^l V(\rho)e^{-\rho/2} - \frac{1}{2}\rho^{l+1}V'(\rho)e^{-\rho/2} + \frac{3}{4}\rho^{l+1}V(\rho)e^{-\rho/2}$$

$$y''(\rho) = \left[\frac{l(l+1)}{\rho^2} - \frac{(l+1)}{\rho} + \frac{1}{4}\right]y(\rho) + (2l+2-\rho)\rho^l V'(\rho)e^{-\rho/2} + \rho^{l+1}V''(\rho)e^{-\rho/2}$$

Substitute into the given differential equation, we get

$$\rho V'' + (2l+2-\rho)V' + (n-l-1)V = 0$$

When $l = n-1$, we get $\rho V'' + (2n-\rho)V' = 0$

Clearly, $V(\rho) = \text{constant}$ is a solution, we thus have

$$y(\rho) = \text{const}\cdot\rho^{l+1}e^{-\rho/2}, \ \rho = 2\kappa r = \frac{2r}{na_0}$$

1(c) $P_n(r) = r^2\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left|\psi_{nlm}(\vec{x})\right|^2$

$$= r^2\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left(\frac{2}{na_0}\right)^3 \frac{1}{(2n)!}\rho^{2n-2}e^{-\rho}\left|Y_l^m(\theta,\phi)\right|^2$$

Since $\rho = \frac{2r}{na_0}$, $P_n(r) = \int_0^\pi \sin\theta d\theta \left(\frac{2}{na_0}\right)\frac{1}{(2n)!}\rho^{2n}e^{-\rho} = \frac{4}{na_0}\frac{1}{(2n)!}\rho^{2n}e^{-\rho}$

$$\frac{dP_n}{dr} = \frac{4}{na_0}\frac{1}{(2n)!}(2n\rho^{2n-1}e^{-\rho} - \rho^{2n}e^{-\rho})$$

When $\frac{dP_n}{dr} = 0$, $\rho = 2n \Rightarrow \frac{2r}{na_0} = 2n$

$$\therefore r = n^2 a_0 \text{ (shown)}$$

2(a) Hamiltonian of 3D harmonic oscillator: **(Refer to lecture notes for more details)**

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2m} + \frac{1}{2}m\omega^2(x_1^2 + x_2^2 + x_3^2) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2$$

The time-independent Schrodinger equation for 3D harmonic oscillator is:

$$\left[\frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2\right]\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

We can transform the above equation into 1D radial equation, just as the case for hydrogen atom.

By considering the boundary conditions, we can obtain the radial wavefunction as a product of different functions.

By using power series method, we can obtain the solution between 0 and infinity.

Since the power series will blow up, we need to truncate the series at a particular term.

Once truncated, we can compare the Laguerre polynomial in 3D harmonic oscillator and the polynomial for hydrogen atom.

The principal quantum number of the 3D harmonic oscillator can be obtained in terms of orbital angular momentum quantum number.
By substituting the energy term of $E=(n+\frac{3}{2})\hbar\omega$, we are able to get the orbital angular momentum quantum number to be n, $n-2, n-4, ..., 0$ or 1.

2(b)(i) Possible values of $l^2 = l(l+1)\hbar^2 = 1(1+1)\hbar^2 = 2\hbar^2$
Probability = 1

2(b)(ii) Possible values of $J = \frac{1}{2}, \frac{3}{2}$

Possible values of $J^2 = J(J+1)\hbar^2 = \frac{3}{4}\hbar^2, \frac{15}{4}\hbar^2$

$$|1,0\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\left|\frac{3}{2},\frac{1}{2}\right\rangle - \sqrt{\frac{1}{3}}\left|\frac{1}{2},\frac{1}{2}\right\rangle \qquad |1,1\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}\left|\frac{3}{2},\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

$$\frac{1}{\sqrt{3}}|1,0\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}|1,1\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \frac{\sqrt{2}}{3}\left|\frac{3}{2},\frac{1}{2}\right\rangle - \frac{1}{3}\left|\frac{1}{2},\frac{1}{2}\right\rangle + \frac{\sqrt{2}}{3}\left|\frac{3}{2},\frac{1}{2}\right\rangle + \frac{2}{3}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$
$$= 2\frac{\sqrt{2}}{3}\left|\frac{3}{2},\frac{1}{2}\right\rangle + \frac{1}{3}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

Probability to get $\frac{3}{4}\hbar^2 = \frac{1}{9}$ Probability to get $\frac{15}{4}\hbar^2 = \frac{8}{9}$

2(b)(iii) Probability density = $\frac{1}{3}|R(r)|^2 \int_0^{2\pi}\int_0^{\pi} |Y_1^0(\theta,\phi)|^2 \, d\phi d\theta = \frac{1}{3}|R(r)|^2$

2(c) Possible values of $j = |j_1 - j_2|, |j_1 - j_2| + 1, |j_1 - j_2| + 2, \ldots, j_1 + j_2$

$$|j_1, j_2, j, m\rangle = \sum_{m_1 m_2} |j_1, j_2, m_1, m_2\rangle\langle j_1, j_2, m_1, m_2 | j, m\rangle$$

Interchange (j_1, m_1) and (j_2, m_2),

$$|j_1, j_2, j, m\rangle' = \sum_{m_2 m_1} |j_2, j_1, m_2, m_1\rangle\langle j_2, j_1, m_2, m_1 | j, m\rangle$$
$$= \sum_{m_1 m_2} |j_1, j_2, m_1, m_2\rangle\langle j_2, j_1, m_2, m_1 | j, m\rangle$$
$$= \sum_{m_1 m_2} |j_1, j_2, m_1, m_2\rangle(-1)^{j-(j_1+j_2)}\langle j_2, j_1, m_2, m_1 | j, m\rangle$$
$$= (-1)^{j-(j_1+j_2)}|j_1, j_2, j, m\rangle = (-1)^{j+j_1+j_2-2(j_1+j_2)}|j_1, j_2, j, m\rangle$$
$$= (-1)^{j+j_1+j_2}|j_1, j_2, j, m\rangle \qquad \because (-1)^{-2(j_1+j_2)} = 1$$

Since $(-1)^{j+j_1+j_2}$ can be either equal to +1 or -1, the eigenstates of the total resultant momentum are either symmetrical or anti-symmetrical against the interchange of m_1 and m_2. (shown)

3(i) $R_u(\varepsilon)=1+\varepsilon\hat{u}\times+\frac{1}{2!}\varepsilon^2\hat{u}\times\hat{u}\times$ $\qquad R_v(\varepsilon)=1+\varepsilon\hat{v}\times+\frac{1}{2!}\varepsilon^2\hat{v}\times\hat{v}\times$

$R_u^{-1}(\varepsilon)=1-\varepsilon\hat{u}\times+\frac{1}{2!}\varepsilon^2\hat{u}\times\hat{u}\times$ $\qquad R_v^{-1}(\varepsilon)=1-\varepsilon\hat{v}\times+\frac{1}{2!}\varepsilon^2\hat{v}\times\hat{v}\times$

$$R_v(\varepsilon)R_u(\varepsilon)=(1+\varepsilon\hat{v}\times+\frac{1}{2!}\varepsilon^2\hat{v}\times\hat{v}\times)(1+\varepsilon\hat{u}\times+\frac{1}{2!}\varepsilon^2\hat{u}\times\hat{u}\times)$$

$$=\left[1+\varepsilon(\hat{v}\times+\hat{u}\times)+\varepsilon^2\left(\hat{v}\times\hat{u}\times+\frac{1}{2}\hat{v}\times\hat{v}\times+\hat{u}\times\hat{u}\times\right)\right]+O\left(\varepsilon^3\right)$$

$R_u^{-1}R_vR_u$

$$=\left(1-\varepsilon\hat{u}\times+\frac{1}{2!}\varepsilon^2\hat{u}\times\hat{u}\times\right)\left[1+\varepsilon(\hat{v}\times+\hat{u}\times)+\varepsilon^2\left(\hat{v}\times\hat{u}\times+\frac{1}{2}\hat{v}\times\hat{v}\times+\frac{1}{2}\hat{u}\times\hat{u}\times\right)+O\left(\varepsilon^3\right)\right]$$

$$=1+\varepsilon\hat{v}\times\varepsilon^2\left(\hat{v}\times\hat{u}\times+\frac{1}{2}\hat{v}\times\hat{v}\times-\hat{u}\times\hat{v}\times\right)+O\left(\varepsilon^3\right)$$

$$R_v^{-1}R_u^{-1}R_vR_u=\left(1-\varepsilon\hat{v}\times+\frac{1}{2!}\varepsilon^2\hat{v}\times\hat{v}\times\right)\left[1+\varepsilon\hat{v}\times+\varepsilon^2\left(\hat{v}\times\hat{u}\times+\frac{1}{2}\hat{v}\times\hat{v}\times-\hat{u}\times\hat{v}\times\right)+O\left(\varepsilon^3\right)\right]$$

$$=1+\varepsilon^2\left[\hat{v}\times\hat{u}\times-\hat{u}\times\hat{v}\times\right]+O(\varepsilon^3)$$

$$R_v^{-1}R_u^{-1}R_vR_u\vec{x}=\vec{x}+\varepsilon^2\left[\hat{v}\times\hat{u}\times-\hat{u}\times\hat{v}\times\right]\vec{x}+O\left(\varepsilon^3\right)\vec{x}=\vec{x}+\varepsilon^2\left[(\hat{v}\cdot\vec{x})\hat{u}-(\hat{u}\cdot\vec{x})\hat{v}\right]+O\left(\varepsilon^3\right)\vec{x}$$

$$R_w\left(-\varepsilon^2\right)\vec{x}=\vec{x}-\varepsilon^2\hat{w}\times\vec{x}=\vec{x}+\varepsilon^2\vec{x}\times\hat{w}=\vec{x}+\varepsilon^2\vec{x}\times(\hat{u}\times\hat{v})=\vec{x}+\varepsilon^2\left[(\hat{v}\cdot\vec{x})\hat{u}-(\hat{u}\cdot\vec{x})\hat{v}\right]$$

Since $R_v^{-1}R_u^{-1}R_vR_u=R$, from the above results, R differs from R_w only by terms higher order than ε^2. (shown)

3(ii) $R_u(\phi)=e^{-i\phi J_u/\hbar}$

$R_u(\varepsilon)=e^{-i\varepsilon J_u/\hbar}=1-\frac{i\varepsilon J_u}{\hbar}-\frac{\varepsilon^2J_u^2}{2\hbar^2}$ $\qquad R_v(\varepsilon)=e^{-i\varepsilon J_v/\hbar}=1-\frac{i\varepsilon J_v}{\hbar}-\frac{\varepsilon^2J_v^2}{2\hbar^2}$

$R_u^{-1}(\varepsilon)=e^{i\varepsilon J_u/\hbar}=1+\frac{i\varepsilon J_u}{\hbar}-\frac{\varepsilon^2J_u^2}{2\hbar^2}$ $\qquad R_v^{-1}(\varepsilon)=e^{i\varepsilon J_v/\hbar}=1+\frac{i\varepsilon J_v}{\hbar}-\frac{\varepsilon^2J_v^2}{2\hbar^2}$

$$R=R_v^{-1}(\varepsilon)R_u^{-1}(\varepsilon)R_v(\varepsilon)R_u(\varepsilon)=R_v^{-1}(\varepsilon)R_u^{-1}(\varepsilon)(1-\frac{i\varepsilon J_v}{\hbar}-\frac{\varepsilon^2J_v^2}{2\hbar^2})(1-\frac{i\varepsilon J_u}{\hbar}-\frac{\varepsilon^2J_u^2}{2\hbar^2})$$

$$=R_v^{-1}(\varepsilon)(1+\frac{i\varepsilon J_u}{\hbar}-\frac{\varepsilon^2J_u^2}{2\hbar^2})(1-\frac{i\varepsilon J_u}{\hbar}-\frac{\varepsilon^2J_u^2}{2\hbar^2}-\frac{i\varepsilon J_v}{\hbar}-\frac{\varepsilon^2J_v^2}{2\hbar^2}-\varepsilon^2\frac{J_vJ_u}{\hbar^2})$$

$$=(1+\frac{i\varepsilon J_v}{\hbar}-\frac{\varepsilon^2J_v^2}{2\hbar^2})(1-\frac{i\varepsilon J_v}{\hbar}-\varepsilon^2\frac{J_vJ_u}{\hbar^2}+\varepsilon^2\frac{J_uJ_v}{\hbar^2}-\frac{\varepsilon^2J_v^2}{2\hbar^2})$$

$$=1+\frac{\varepsilon^2}{\hbar^2}\left[J_u,J_v\right]$$

$$R_w(-\varepsilon^2) = e^{i\varepsilon^2 J_w/\hbar} = 1 + i\varepsilon^2 J_w/\hbar$$

Since $R = R_w(-\varepsilon^2)$, $\quad 1 + \dfrac{\varepsilon^2}{\hbar^2}[J_u, J_v] = 1 + i\varepsilon^2 J_w/\hbar$

$$[J_u, J_v] = i\hbar J_w \text{ (shown)}$$

4(a) Consider the Hamiltonian of a pair of particle and its anti-particle, e.g. electron and positron. This Hamiltonian commutes with the permutation operator, but the states need not be symmetrized or antisymmetrized.

4(b)(i) Identical bosons:

Ground state: $\psi_{11}(x_1, x_2) = \dfrac{2}{b}\sin(\dfrac{\pi x_1}{b})\sin(\dfrac{\pi x_2}{b})$

Energy of ground state, $E_{11} = 2\left(\dfrac{\hbar^2\pi^2}{2mb^2}\right)$

1st excited state: $\psi_{12}(x_1, x_2) = \dfrac{\sqrt{2}}{b}\left[\sin(\dfrac{\pi x_1}{b})\sin(\dfrac{2\pi x_2}{b}) + \sin(\dfrac{2\pi x_1}{b})\sin(\dfrac{\pi x_2}{b})\right]$

Energy of 1st excited state, $E_{12} = 5\left(\dfrac{\hbar^2\pi^2}{2mb^2}\right)$

2nd excited state: $\psi_{22}(x_1, x_2) = \dfrac{2}{b}\sin(\dfrac{2\pi x_1}{b})\sin(\dfrac{2\pi x_2}{b})$

Energy of 2nd excited state, $E_{22} = 8\left(\dfrac{\hbar^2\pi^2}{2mb^2}\right)$

4(b)(ii) Identical fermions:

Ground state: $\psi_{12}(x_1, x_2) = \dfrac{\sqrt{2}}{b}\left[\sin(\dfrac{\pi x_1}{b})\sin(\dfrac{2\pi x_2}{b}) - \sin(\dfrac{2\pi x_1}{b})\sin(\dfrac{\pi x_2}{b})\right]$

Energy of ground state, $E_{12} = 5\left(\dfrac{\hbar^2\pi^2}{2mb^2}\right)$

1st excited state: $\psi_{13}(x_1, x_2) = \dfrac{\sqrt{2}}{b}\left[\sin(\dfrac{\pi x_1}{b})\sin(\dfrac{3\pi x_2}{b}) - \sin(\dfrac{3\pi x_1}{b})\sin(\dfrac{\pi x_2}{b})\right]$

Energy of 1st excited state, $E_{13} = 10\left(\dfrac{\hbar^2\pi^2}{2mb^2}\right)$

2nd excited state: $\psi_{23}(x_1, x_2) = \dfrac{\sqrt{2}}{b}\left[\sin(\dfrac{2\pi x_1}{b})\sin(\dfrac{3\pi x_2}{b}) - \sin(\dfrac{3\pi x_1}{b})\sin(\dfrac{2\pi x_2}{b})\right]$

Energy of 2nd excited state, $E_{23} = 13\left(\dfrac{\hbar^2\pi^2}{2mb^2}\right)$

Ground state wavefunction of 3 identical fermions:

$$\psi_{123} = \sqrt{\frac{2}{3b^3}}\left[\sin\left(\frac{\pi x_1}{b}\right)\sin\left(\frac{2\pi x_2}{b}\right)\sin\left(\frac{3\pi x_3}{b}\right) + \sin\left(\frac{2\pi x_1}{b}\right)\sin\left(\frac{3\pi x_2}{b}\right)\sin\left(\frac{\pi x_3}{b}\right) + \right.$$

$$\sin\left(\frac{3\pi x_1}{b}\right)\sin\left(\frac{\pi x_2}{b}\right)\sin\left(\frac{2\pi x_3}{b}\right)-\sin\left(\frac{\pi x_1}{b}\right)\sin\left(\frac{3\pi x_2}{b}\right)\sin\left(\frac{2\pi x_3}{b}\right)-$$
$$\sin\left(\frac{2\pi x_1}{b}\right)\sin\left(\frac{\pi x_2}{b}\right)\sin\left(\frac{3\pi x_3}{b}\right)-\sin\left(\frac{3\pi x_1}{b}\right)\sin\left(\frac{2\pi x_2}{b}\right)\sin\left(\frac{\pi x_3}{b}\right)\Bigg]$$

4(c)
$$\left\langle S_a^{(1)}S_b^{(2)}\right\rangle=\left\langle 0,0\middle|S_a^{(1)}S_b^{(2)}\middle|0,0\right\rangle$$
$$=\frac{1}{2}\left(\left\langle\frac{1}{2},-\frac{1}{2}\right|-\left\langle-\frac{1}{2},\frac{1}{2}\right|\right)S_a^{(1)}S_b^{(2)}\left(\left|\frac{1}{2},-\frac{1}{2}\right\rangle-\left|-\frac{1}{2},\frac{1}{2}\right\rangle\right)$$
$$=\frac{1}{2}\left\langle\frac{1}{2},-\frac{1}{2}\middle|S_a^{(1)}S_b^{(2)}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle+\frac{1}{2}\left\langle-\frac{1}{2},\frac{1}{2}\middle|S_a^{(1)}S_b^{(2)}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle$$

Taking $S_a^{(1)}=S_3^{(1)}$, let $\hat{b}$ be the vector on x_1x_3 plane, $S_b^{(2)}=S_3^{(2)}\cos\theta+S_1^{(2)}\sin\theta$

$$\left\langle S_a^{(1)}S_b^{(2)}\right\rangle=\frac{1}{2}\left\langle\frac{1}{2},-\frac{1}{2}\middle|S_3^{(1)}(S_3^{(2)}\cos\theta+S_1^{(2)}\sin\theta)\middle|\frac{1}{2},-\frac{1}{2}\right\rangle$$
$$+\frac{1}{2}\left\langle-\frac{1}{2},\frac{1}{2}\middle|S_3^{(1)}(S_3^{(2)}\cos\theta+S_1^{(2)}\sin\theta)\middle|-\frac{1}{2},\frac{1}{2}\right\rangle$$
$$\left\langle\frac{1}{2},-\frac{1}{2}\middle|S_3^{(1)}(S_3^{(2)}\cos\theta+S_1^{(2)}\sin\theta)\middle|\frac{1}{2},-\frac{1}{2}\right\rangle=-\frac{\hbar^2}{4}\cos\theta+\frac{\hbar^2}{4}\sin\theta\left\langle\frac{1}{2},-\frac{1}{2}\middle|\frac{1}{2},\frac{1}{2}\right\rangle$$
$$=-\frac{\hbar^2}{4}\cos\theta$$
$$\left\langle-\frac{1}{2},\frac{1}{2}\middle|S_3^{(1)}(S_3^{(2)}\cos\theta+S_1^{(2)}\sin\theta)\middle|-\frac{1}{2},\frac{1}{2}\right\rangle=-\frac{\hbar^2}{4}\cos\theta-\frac{\hbar^2}{4}\sin\theta\left\langle-\frac{1}{2},\frac{1}{2}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle$$
$$=-\frac{\hbar^2}{4}\cos\theta$$
$$\left\langle S_a^{(1)}S_b^{(2)}\right\rangle=\frac{1}{2}\left(-\frac{\hbar^2}{4}\cos\theta\right)+\frac{1}{2}\left(-\frac{\hbar^2}{4}\cos\theta\right)=-\frac{\hbar^2}{4}\cos\theta\ \text{(shown)}$$