PH30030: Quantum Mechanics   Problems Sheet 3 Solutions

1. Follow through the derivation in the lecture notes.

2. For a spherically symmetric state we require $4\pi \int_0^\infty dr\, r^2 |u|^2 = 1$, so in this case we require

   $4\pi A^2 \int_0^a dr \sin^2\left(\frac{n\pi r}{a}\right) = 1$ (note that the wavefunction is zero outside the well).

   By using the useful integrals from problems sheet 1 we find that the integral equals $\frac{a}{2}$, so

   $A = \sqrt{\frac{1}{2\pi a}}$.

3. (a) The energy eigenvalues are given by $E_n = -\frac{1}{n^2}\frac{\mu e^4}{32\pi^2\epsilon_0{}^2\hbar^2}$. So the discrepancy in the value of E_n caused by using m_e instead of μ

   $$\frac{m_e - \mu}{m_e} = 1 - \frac{m_p m_e}{\left(m_p + m_e\right) m_e} = \frac{1.672623\times 10^{-27}}{1.672623\times 10^{-27} + 9.109384\times 10^{-31}} = 0.000544$$

   or 0.0544%, where m_p is the proton mass.

   (b) The energy of the emitted photon $E = \frac{hc}{\lambda} = \left|E_f - E_i\right|$. So, the wavelength λ is given by

   $$\frac{1}{\lambda} = \frac{1}{hc}\frac{\mu}{m_e}\frac{m_e e^4}{32\pi^2\epsilon_0{}^2\hbar^2}\left|\frac{1}{n_f^2} - \frac{1}{n_i^2}\right| \equiv \frac{\mu}{m_e} R \left|\frac{1}{n_f^2} - \frac{1}{n_i^2}\right|$$

   where $R = \frac{m_e e^4}{32\pi^2\epsilon_0{}^2\hbar^2 hc} = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}$ = 1.097375×10^7 m^{-1} is the Rydberg constant.

   For hydrogen, the reduced mass $\mu = 9.104426 \times 10^{-31}$ kg. Hence, for n_f = 2 and n_i = 3, the wavelength of emitted light $\lambda = 6.565\times 10^{-7}\,\text{m}$.
   For deuterium, the reduced mass $\mu = 9.106904 \times 10^{-31}$ kg. Hence, for n_f = 2 and n_i = 3, the wavelength of emitted light $\lambda = 6.563\times 10^{-7}\,\text{m}$.
   Differences between the spectra of hydrogen and deuterium led to the discovery of deuterium by Urey and collaborators in 1932.

   (c) For positronium, $E_n = -\frac{1}{n^2}\frac{\mu e^4}{32\pi^2\epsilon_0{}^2\hbar^2}$ with reduced mass $\mu = m_e/2$. So the binding energy (corresponding to minimum in potential well with n = 1) is $E_1 = -\frac{m_e e^4}{64\pi^2\epsilon_0{}^2\hbar^2}$ = –6.8 eV.

   (d) The reduced mass $\mu = 1.692908 \times 10^{-28}$ kg. For n_f = 1 and n_i = 2, the wavelength of emitted light $\lambda = 6.538\times 10^{-10}\,\text{m}$.

4. The expectation value of the kinetic energy $\left\langle \hat{T} \right\rangle = \iiint d^3r\, u(r,\theta,\phi)\left(-\frac{\hbar^2}{2\mu}\nabla^2\right)u(r,\theta,\phi)$.

For $\ell = 0$, $u(r,\theta,\phi)$ has no θ or ϕ dependence.

So, $\nabla^2 u_{100}(r,\theta,\phi) = \frac{1}{r^2}\left(\frac{d}{dr}r^2\frac{d}{dr}\right)u_{100}(r,\theta,\phi)$ (in spherical polars) and $d^3r = 4\pi r^2 dr$.

Hence, $\left\langle \hat{T} \right\rangle = -\frac{\hbar^2}{2\mu}\frac{1}{\pi a_0^3}4\pi\int_0^\infty dr \exp(-r/a_0)\left(\frac{d}{dr}r^2\frac{d}{dr}\right)\exp(-r/a_0)$.

Doing the differentiations of $\exp(-r/a_0)$ leads to the integral in this expression becoming two integrals: $\frac{1}{a_0^2}\int_0^\infty dr\, r^2 \exp(-2r/a_0) - \frac{2}{a_0}\int_0^\infty dr\, r \exp(-2r/a_0)$.

From the useful integrals on problems sheet 1 we can evaluate these to give $\frac{a_0}{4} - \frac{a_0}{2} = -\frac{a_0}{4}$.

The expectation of the kinetic energy is therefore $\left\langle \hat{T} \right\rangle = \frac{\hbar^2}{2\mu}\frac{1}{a_0^2}$.

The expectation value of the potential energy is given by $\left\langle \hat{V} \right\rangle = \iiint d^3r\, u(r,\theta,\phi)V(r)u(r,\theta,\phi)$.

In this case $V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$, so $\left\langle \hat{V} \right\rangle = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi a_0^3}4\pi\int_0^\infty dr\, r \exp(-2r/a_0)$.

Doing the integral gives $-\frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi a_0^3}4\pi\frac{a_0^2}{4} = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0}$.

From the definition of the Bohr radius, we know that $a_0 = \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{\mu}$, so the expectation of the potential energy can be written as $\left\langle \hat{V} \right\rangle = -\frac{\hbar^2}{2\mu}\frac{2}{a_0^2}$.

The sum of the expectation values

$\left\langle \hat{H} \right\rangle = \left\langle \hat{T} \right\rangle + \left\langle \hat{V} \right\rangle = \frac{\hbar^2}{2\mu}\frac{1}{a_0^2} - \frac{\hbar^2}{2\mu}\frac{2}{a_0^2} = -\frac{\hbar^2}{2\mu}\frac{1}{a_0^2} = -\frac{\mu e^4}{32\pi^2\epsilon_0{}^2\hbar^2}$, which is the energy of the $1s$ state.

5. $\hat{P}_{12}$ is Hermitian if $\left\langle \phi(x_1,x_2) \middle| \hat{P}_{12}\phi(x_1,x_2) \right\rangle = \left\langle \hat{P}_{12}\phi(x_1,x_2) \middle| \phi(x_1,x_2) \right\rangle$.

Now

$$\left\langle \phi(x_1,x_2) \middle| \hat{P}_{12}\phi(x_1,x_2) \right\rangle = \int dx_1 dx_2 \phi^*(x_1,x_2)\hat{P}_{12}\phi(x_1,x_2) = \int dx_1 dx_2 \phi^*(x_1,x_2)\phi(x_2,x_1).$$

Changing the dummy variables to $y_1 = x_2$ and $y_2 = x_1$ gives.

$$\int dx_1 dx_2 \phi^*(x_1,x_2)\phi(x_2,x_1) = \int dy_1 dy_2 \phi^*(y_2,y_1)\phi(y_1,y_2) = \int dy_1 dy_2 \left[\hat{P}_{12}\phi(y_1,y_2)\right]^* \phi(y_1,y_2)$$

Changing the dummy variables to $y_1 = x_1$ and $y_2 = x_2$ gives

$$\int dy_1 dy_2 \left[\hat{P}_{12}\phi(y_1,y_2)\right]^* \phi(y_1,y_2) = \int dx_1 dx_2 \left[\hat{P}_{12}\phi(x_1,x_2)\right]^* \phi(x_1,x_2) = \left\langle \hat{P}_{12}\phi(x_1,x_2) \middle| \phi(x_1,x_2) \right\rangle$$

So,

$$\left\langle \phi(x_1,x_2) \middle| \hat{P}_{12}\phi(x_1,x_2) \right\rangle = \left\langle \hat{P}_{12}\phi(x_1,x_2) \middle| \phi(x_1,x_2) \right\rangle$$

as required.

Alternatively: -

$$\left\langle \phi(x_1,x_2) \middle| \hat{P}_{12}\phi(x_1,x_2) \right\rangle = \int dx_1 dx_2 \phi^*(x_1,x_2)\hat{P}_{12}\phi(x_1,x_2) = \int dx_1 dx_2 \phi^*(x_1,x_2)\phi(x_2,x_1). \qquad (1)$$

Also,

$$\left\langle \hat{P}_{12}\phi(x_1,x_2) \middle| \phi(x_1,x_2) \right\rangle = \int dx_1 dx_2 \left[\hat{P}_{12}\phi(x_1,x_2)\right]^* \phi(x_1,x_2) = \int dx_1 dx_2 \phi^*(x_2,x_1)\phi(x_1,x_2).$$

But x_1 and x_2 are dummy variables, so the last integral can be re-written as

$$\int dx_1 dx_2 \phi^*(x_2,x_1)\phi(x_1,x_2) = \int dx_1 dx_2 \phi^*(x_1,x_2)\phi(x_2,x_1),$$

which is the same as Eq. (1). So,

$$\left\langle \phi(x_1,x_2) \middle| \hat{P}_{12}\phi(x_1,x_2) \right\rangle = \left\langle \hat{P}_{12}\phi(x_1,x_2) \middle| \phi(x_1,x_2) \right\rangle$$

as required.

Alternatively: -

$$\left\langle \phi(x_1,x_2) \middle| \hat{P}_{12}\phi(x_1,x_2) \right\rangle = \int dx_1 dx_2 \phi^*(x_1,x_2)\hat{P}_{12}\phi(x_1,x_2).$$

But x_1 and x_2 are dummy variables, so the last integral can be re-written as

$$\begin{aligned}\int dx_1 dx_2 \phi^*(x_1,x_2)\hat{P}_{12}\phi(x_1,x_2) &= \int dx_1 dx_2 \phi^*(x_2,x_1)\hat{P}_{12}\phi(x_2,x_1) \\ &= \int dx_1 dx_2 \left[\hat{P}_{12}\phi(x_1,x_2)\right]^* \phi(x_1,x_2) \\ &= \left\langle \hat{P}_{12}\phi(x_1,x_2) \middle| \phi(x_1,x_2) \right\rangle\end{aligned}$$

So,

$$\left\langle \phi(x_1,x_2) \middle| \hat{P}_{12}\phi(x_1,x_2) \right\rangle = \left\langle \hat{P}_{12}\phi(x_1,x_2) \middle| \phi(x_1,x_2) \right\rangle$$

as required.

6. The symmetric (+) and anti-symmetric (–) combinations of the particle states are given by $u_\pm\left(\underline{r}_1,\underline{r}_2\right)=A\left[u_a\left(\underline{r}_1\right)u_b\left(\underline{r}_2\right)\pm u_a\left(\underline{r}_2\right)u_b\left(\underline{r}_1\right)\right]$. For normalisation

$$\int d^3r_1 d^3r_2\ u_\pm^* u_\pm = |A|^2 \int d^3r_1 d^3r_2 \left[u_a\left(\underline{r}_1\right)u_b\left(\underline{r}_2\right)\pm u_a\left(\underline{r}_2\right)u_b\left(\underline{r}_1\right)\right]^* \left[u_a\left(\underline{r}_1\right)u_b\left(\underline{r}_2\right)\pm u_a\left(\underline{r}_2\right)u_b\left(\underline{r}_1\right)\right]=1$$

Multiplying out the integrand gives

$$\int d^3r_1 d^3r_2\ u_\pm^* u_\pm =$$
$$|A|^2\,[\int d^3r_1\, u_a^*\left(\underline{r}_1\right)u_a\left(\underline{r}_1\right)\int d^3r_2\, u_b^*\left(\underline{r}_2\right)u_b\left(\underline{r}_2\right)\pm\int d^3r_1\, u_a^*\left(\underline{r}_1\right)u_b\left(\underline{r}_1\right)\int d^3r_2\, u_b^*\left(\underline{r}_2\right)u_a\left(\underline{r}_2\right)$$
$$\pm\int d^3r_1\, u_b^*\left(\underline{r}_1\right)u_a\left(\underline{r}_1\right)\int d^3r_2\, u_a^*\left(\underline{r}_2\right)u_b\left(\underline{r}_2\right)+\int d^3r_1\, u_b^*\left(\underline{r}_1\right)u_b\left(\underline{r}_1\right)\int d^3r_2\, u_a^*\left(\underline{r}_2\right)u_a\left(\underline{r}_2\right)]$$
$$=|A|^2\left[1\pm 0\pm 0+1\right]=2|A|^2=1$$

where we have used the orthonormality of the eigenfunctions: $\int d^3r_i\ u_a^*\left(\underline{r}_i\right)u_b\left(\underline{r}_i\right)=\delta_{ab}$. Hence $A=1/\sqrt{2}$.

If $u_a\left(\underline{r}_i\right)=u_b\left(\underline{r}_i\right)$, then the wavefunction for the antisymmetric state $u_-\left(\underline{r}_1,\underline{r}_2\right)=A\left[u_a\left(\underline{r}_1\right)u_b\left(\underline{r}_2\right)-u_a\left(\underline{r}_2\right)u_b\left(\underline{r}_1\right)\right]=A\left[u_a\left(\underline{r}_1\right)u_a\left(\underline{r}_2\right)-u_a\left(\underline{r}_2\right)u_a\left(\underline{r}_1\right)\right]=0$, i.e., the state does not exist (Pauli exclusion principle).

For the symmetric state, $u_+\left(\underline{r}_1,\underline{r}_2\right)=A\left[u_a\left(\underline{r}_1\right)u_b\left(\underline{r}_2\right)+u_a\left(\underline{r}_2\right)u_b\left(\underline{r}_1\right)\right]$
$=A\left[u_a\left(\underline{r}_1\right)u_a\left(\underline{r}_2\right)+u_a\left(\underline{r}_2\right)u_a\left(\underline{r}_1\right)\right]=A2u_a\left(\underline{r}_1\right)u_a\left(\underline{r}_2\right)$. Normalisation gives

$$\int d^3r_1 d^3r_2\ u_+^* u_+ = 4|A|^2\int d^3r_1 d^3r_2\left[u_a\left(\underline{r}_1\right)u_a\left(\underline{r}_2\right)\right]^*\left[u_a\left(\underline{r}_1\right)u_a\left(\underline{r}_2\right)\right]$$
$$=4|A|^2\int d^3r_1\, u_a^*\left(\underline{r}_1\right)u_a\left(\underline{r}_1\right)\int d^3r_2\, u_a^*\left(\underline{r}_2\right)u_a\left(\underline{r}_2\right)=4|A|^2=1$$

So $A=1/2$.

Particles with symmetric wavefunctions are bosons. Particles with antisymmetric wavefunctions are fermions.

7. (a) From the lecture notes, the composite wavefunction for two distinguishable non-interacting particles in an external field with particle 1 in state a and particle 2 in state b is given by

$u_{ab}\left(x_1,x_2\right)=u_a\left(x_1\right)u_b\left(x_2\right)$ with $E_{ab}=E_a+E_b=\left(n_a^2+n_b^2\right)\dfrac{\hbar^2\pi^2}{2ma^2}$.

The ground state corresponds to $a=b=1$ with $n_a=n_b=1$: -

$u_{11}\left(x_1,x_2\right)=\dfrac{2}{a}\sin\left(\dfrac{\pi x_1}{a}\right)\sin\left(\dfrac{\pi x_2}{a}\right)$ with $E_{11}=2\dfrac{\hbar^2\pi^2}{2ma^2}$

and is non-degenerate. The first excited state corresponds to $n_a=1, n_b=2$ or $n_a=2, n_b=1$: -

$u_{12}\left(x_1,x_2\right)=\dfrac{2}{a}\sin\left(\dfrac{\pi x_1}{a}\right)\sin\left(\dfrac{2\pi x_2}{a}\right)$ with $E_{12}=5\dfrac{\hbar^2\pi^2}{2ma^2}$

$u_{21}\left(x_1,x_2\right)=\dfrac{2}{a}\sin\left(\dfrac{2\pi x_1}{a}\right)\sin\left(\dfrac{\pi x_2}{a}\right)$ with $E_{21}=5\dfrac{\hbar^2\pi^2}{2ma^2}$

Interchanging the particle labels (e.g., 1→2 and 2→1) changes the energy eigenfunction but not change the energy eigenvalue, i.e., the first excited state is doubly degenerate.

(b) For bosons, $u_+(x_1,x_2)=A\left[u_a(x_1)u_b(x_2)+u_a(x_2)u_b(x_1)\right]$.

The ground state corresponds to $a=b=1$ such that the normalisation constant $A=1/2$ (see question 6). Then

$u_{+,\,\text{ground}}=\frac{1}{2}\left[u_1(x_1)u_1(x_2)+u_1(x_2)u_1(x_1)\right]=u_1(x_1)u_1(x_2)=\frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$ with

$E_{+,\,\text{ground}}=2\frac{\hbar^2\pi^2}{2ma^2}$ and is non-degenerate.

For the first excited state the normalisation constant $A=1/\sqrt{2}$ (see question 6) and

$$u_{+,\,\text{1st excited}}=\frac{1}{\sqrt{2}}\left[u_1(x_1)u_2(x_2)+u_1(x_2)u_2(x_1)\right]=\frac{1}{\sqrt{2}}\frac{2}{a}\left[\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right)+\sin\left(\frac{\pi x_2}{a}\right)\sin\left(\frac{2\pi x_1}{a}\right)\right]$$

with $E_{\text{1st excited}}=5\frac{\hbar^2\pi^2}{2ma^2}$. Interchanging the particle labels does not change $u_{+,\,\text{1st excited}}$ so the first excited state is non-degenerate.

(c) For fermions, $u_-(x_1,x_2)=\frac{1}{\sqrt{2}}\left[u_a(x_1)u_b(x_2)-u_a(x_2)u_b(x_1)\right]$.

For $a=b=1$, $u_-=\frac{1}{\sqrt{2}}\left[u_1(x_1)u_1(x_2)-u_1(x_2)u_1(x_1)\right]=0$ so the state does not exist (Pauli exclusion principle). The ground state is given by

$$u_{-,\,\text{ground}}=\frac{1}{\sqrt{2}}\left[u_1(x_1)u_2(x_2)-u_1(x_2)u_2(x_1)\right]=\frac{1}{\sqrt{2}}\frac{2}{a}\left[\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right)-\sin\left(\frac{\pi x_2}{a}\right)\sin\left(\frac{2\pi x_1}{a}\right)\right]$$

with $E_{\text{ground}}=5\frac{\hbar^2\pi^2}{2ma^2}$. In this case, interchanging the particle labels gives $-u_{-,\,\text{ground}}$ i.e. the negative of the original function. $\left|u_{-,\,\text{ground}}\right|^2=\left|-u_{-,\,\text{ground}}\right|^2$, so the probability of locating the particles is unchanged, and the ground state is non-degenerate.

8. For the 1D infinite square well, the potential energy is zero for $0\le x\le a$, and the Hamiltonian for this region is given by $\hat{H}=\hat{T}_1+\hat{T}_2=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2}$. The energy eigenvalues are given by $E_n=n^2\frac{\hbar^2\pi^2}{2ma^2}$.

   (a) For two distinguishable particles $u_{\text{ground}}(x_1,x_2)=u_1(x_1)u_1(x_2)$ (question 7) and $\hat{T}_1u_1(x_1)=E_1u_1(x_1)$ etc. So

$$\begin{aligned}\hat{H}u_{\text{ground}}(x_1,x_2)&=\left(\hat{T}_1+\hat{T}_2\right)u_1(x_1)u_1(x_2)\\&=u_1(x_2)\hat{T}_1u_1(x_1)+u_1(x_1)\hat{T}_2u_1(x_2)\\&=(E_1+E_1)u_1(x_1)u_1(x_2)=E_{\text{ground}}u_1(x_1)u_1(x_2)\end{aligned}$$

   Hence, $E_{\text{ground}}=2E_1=2\frac{\hbar^2\pi^2}{2ma^2}$ as in question 7.

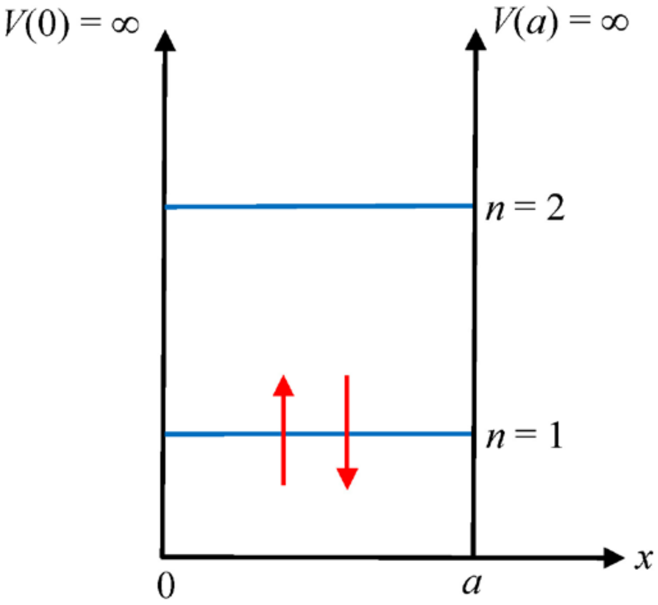
(b) For two identical bosons, $u_{+,\text{ground}} = u_1(x_1)u_1(x_2)$ (question 7), so the answer is the same as for part (a).

(c) For two identical fermions, $u_{-,\text{ground}} = \frac{1}{\sqrt{2}}\left[u_1(x_1)u_2(x_2) - u_1(x_2)u_2(x_1)\right]$ (question 7) and $\hat{T}_1 u_1(x_1) = E_1 u_1(x_1)$, $\hat{T}_1 u_2(x_1) = E_2 u_2(x_1)$ etc. So

$$\begin{aligned}
\hat{H}u_{-,\text{ground}}(x_1,x_2) &= \left(\hat{T}_1 + \hat{T}_2\right)u_{-,\text{ground}}(x_1,x_2) \\
&= \frac{u_2(x_2)}{\sqrt{2}}\hat{T}_1 u_1(x_1) + \frac{u_1(x_1)}{\sqrt{2}}\hat{T}_2 u_2(x_2) \\
&\quad - \left[\frac{u_1(x_2)}{\sqrt{2}}\hat{T}_1 u_2(x_1) + \frac{u_2(x_1)}{\sqrt{2}}\hat{T}_2 u_1(x_2)\right] \\
&= (E_1 + E_2)\frac{u_1(x_1)u_2(x_2)}{\sqrt{2}} - (E_2 + E_1)\frac{u_1(x_2)u_2(x_1)}{\sqrt{2}} \\
&= (E_1 + E_2)u_{-,\text{ground}} = E_{\text{ground}}u_{-,\text{ground}}
\end{aligned}$$

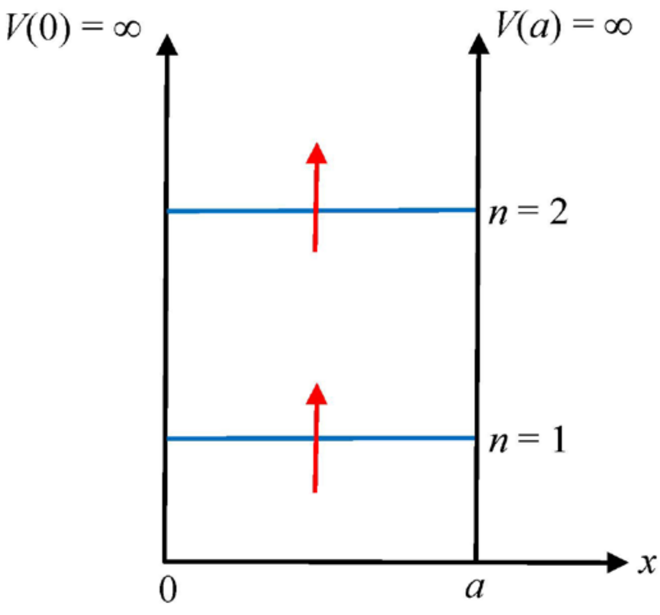
Hence, $E_{\text{ground}} = E_1 + E_2 = 5\frac{\hbar^2\pi^2}{2ma^2}$ as in question 7.

9. If the spins are anti-parallel, the total spin $S = 0$. The overall eigenfunction $\phi(1,2) = u_+(1,2)\chi_{00}(1,2)$ has both a spatially dependent part $u_+(1,2)$ and a spin dependent part $\chi_{00}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \alpha_2\beta_1]$. The ground state corresponds to $a = b = 1$, such that $u_+(1,2) = \frac{1}{2}\left[u_1(x_1)u_1(x_2) + u_1(x_2)u_1(x_1)\right] = u_1(x_1)u_1(x_2)$ which is finite (for the normalisation constant see question 6).



If the spins are parallel, the total spin $S = 1$. The overall eigenfunction $\phi(1,2) = u_-(1,2)\chi_{1M_S}(1,2)$ has both a spatially dependent part $u_-(1,2)$ and a spin dependent part $\chi_{1M_S}(1,2)$ with $M_S = -1, 0 \text{ or } 1$. The ground state corresponds to one electron in the state with n = 1 and the other electron in the state with n = 2 (see question 7).

$u_{-,\text{ ground}} = \frac{1}{\sqrt{2}}\left[u_1(x_1)u_2(x_2) - u_1(x_2)u_2(x_1)\right]$.



10. Orthonormality: $\int dx_i\, u_a^*(x_i)\, u_b(x_i) = \delta_{ab}$

(a) For two distinguishable particles, $u(x_1, x_2) = u_a(x_1)u_b(x_2)$.

$$\begin{aligned}\langle x_1^2\rangle &= \iint u_a^*(x_1)u_b^*(x_2)\,x_1^2 u_a(x_1)u_b(x_2)\,dx_1dx_2\\ &= \int u_a^*(x_1)\,x_1^2 u_a(x_1)\,dx_1 \int |u_b(x_2)|^2 dx_2\\ &= \int u_a^*(x_1)\,x_1^2 u_a(x_1)\,dx_1 \equiv \langle x^2\rangle_a\end{aligned}$$

where $\langle x^2\rangle_a$ is the expectation value of x^2 for the one-particle state $u_a(x)$.

Similarly, $\langle x_2^2\rangle = \int u_b^*(x_2)\,x_2^2 u_b(x_2)\,dx_1 \equiv \langle x^2\rangle_b$,

and

$\langle x_1x_2\rangle = \int u_a^*(x_1)\,x_1 u_a(x_1)\,dx_1 \int u_b^*(x_2)\,x_2 u_b(x_2)\,dx_2 \equiv \langle x\rangle_a \langle x\rangle_b$.

So, for distinguishable particles,

$$\begin{aligned}\left\langle (x_1 - x_2)^2 \right\rangle_{\text{distinguishable}} &= \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1x_2\rangle\\ &= \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b\end{aligned} \quad . \tag{1}$$

(b) & (c): For two identical bosons (+) or fermions (–),

$u_\pm(x_1,x_2)=\frac{1}{\sqrt{2}}\left[u_a(x_1)u_b(x_2)\pm u_a(x_2)u_b(x_1)\right]$. So

$$\langle x_1^2\rangle=\iint u_\pm^*(x_1,x_2)\,x_1^2u_\pm(x_1,x_2)\,dx_1dx_2$$

$$=\frac{1}{2}\begin{bmatrix}\int x_1^2|u_a(x_1)|^2dx_1\int|u_b(x_2)|^2dx_2\\ +\int x_1^2|u_b(x_1)|^2dx_1\int|u_a(x_2)|^2dx_2\\ \pm\int x_1^2u_a(x_1)^*u_b(x_1)dx_1\int u_b(x_2)^*u_a(x_2)dx_2\\ \pm\int x_1^2u_b(x_1)^*u_a(x_1)dx_1\int u_a(x_2)^*u_b(x_2)dx_2\end{bmatrix}$$

$$=\frac{1}{2}\left[\langle x^2\rangle_a+\langle x^2\rangle_b\pm0\pm0\right]=\frac{1}{2}\left[\langle x^2\rangle_a+\langle x^2\rangle_b\right]$$

Similarly, $\langle x_2^2\rangle=\frac{1}{2}\left[\langle x^2\rangle_b+\langle x^2\rangle_a\right]$ as expected (the particles are indistinguishable!)

Also

$$\langle x_1x_2\rangle=\iint u_\pm^*(x_1,x_2)\,x_1x_2u_\pm(x_1,x_2)\,dx_1dx_2$$

$$=\frac{1}{2}\begin{bmatrix}\int x_1|u_a(x_1)|^2dx_1\int x_2|u_b(x_2)|^2dx_2\\ +\int x_1|u_b(x_1)|^2dx_1\int x_2|u_a(x_2)|^2dx_2\\ \pm\int x_1u_a(x_1)^*u_b(x_1)dx_1\int x_2u_b(x_2)^*u_a(x_2)dx_2\\ \pm\int x_1u_b(x_1)^*u_a(x_1)dx_1\int x_2u_a(x_2)^*u_b(x_2)dx_2\end{bmatrix}$$

$$=\frac{1}{2}\left[\langle x\rangle_a\langle x\rangle_b+\langle x\rangle_b\langle x\rangle_a\pm\langle x\rangle_{ab}\langle x\rangle_{ba}\pm\langle x\rangle_{ba}\langle x\rangle_{ab}\right]$$

$$=\langle x\rangle_a\langle x\rangle_b\pm\langle x\rangle_{ab}\langle x\rangle_{ba}=\langle x\rangle_a\langle x\rangle_b\pm\left|\langle x\rangle_{ab}\right|^2$$

where $\langle x\rangle_{ab}\equiv\int xu_a(x)^*u_b(x)dx$ such that $\langle x\rangle_{ab}^*=\int xu_a(x)u_b(x)^*dx=\langle x\rangle_{ba}$.

Hence

$$\begin{aligned}\left\langle(x_1-x_2)^2\right\rangle_\pm&=\langle x_1^2\rangle+\langle x_2^2\rangle-2\langle x_1x_2\rangle\\&=\langle x^2\rangle_a+\langle x^2\rangle_b-2\langle x\rangle_a\langle x\rangle_b\mp2\left|\langle x\rangle_{ab}\right|^2\end{aligned}\qquad(2)$$

A comparison of equations (1) and (2) shows that

$$\left\langle(x_1-x_2)^2\right\rangle_\pm=\left\langle(x_1-x_2)^2\right\rangle_{\text{distinguishable}}\mp2\left|\langle x\rangle_{ab}\right|^2$$

So identical bosons (the upper sign) tend to be closer together, and identical fermions (the lower sign) tend to be further apart, than two distinguishable particles in the same two states. The system behaves as if there were a force of attraction between identical bosons and a force of repulsion between identical fermions. We call it the exchange force, even though it is not really a force at all (see Griffiths & Schroeter 2018, chapter 5). The exchange force has no classical counterpart.

Note that $\left\langle (x_1 - x_2)^2 \right\rangle_{\pm} = \left\langle (x_1 - x_2)^2 \right\rangle_{\text{distinguishable}}$ if $\langle x \rangle_{ab} = \int x u_a(x)^* u_b(x) dx = 0$ i.e. if there is no overlap between $u_a(x)$ and $u_b(x)$. So, if the particles are far enough apart, we can treat them as distinguishable: An electron in New York is distinguishable from an electron in London!

11. Use the Pauli matrices to find the effect of the different operators on α_i and β_i: -

$$\hat{S}_{xi}\alpha_i = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\beta_i$$

$$\hat{S}_{xi}\beta_i = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\alpha_i$$

$$\hat{S}_{yi}\alpha_i = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ i \end{pmatrix} = i\frac{\hbar}{2}\beta_i$$

$$\hat{S}_{yi}\beta_i = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} -i \\ 0 \end{pmatrix} = -i\frac{\hbar}{2}\alpha_i$$

$$\hat{S}_{zi}\alpha_i = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\alpha_i$$

$$\hat{S}_{zi}\beta_i = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}\beta_i$$

So, α_i and β_i are eigenfunctions of $\hat{S}_{zi}$, but not $\hat{S}_{xi}$ nor $\hat{S}_{yi}$.

12. The operators are given by $\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\left(\hat{S}_{x1}\hat{S}_{x2} + \hat{S}_{y1}\hat{S}_{y2} + \hat{S}_{z1}\hat{S}_{z2}\right)$ and $\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$.

$\hat{S}_1^2 = \hat{S}_{x1}^2 + \hat{S}_{y1}^2 + \hat{S}_{z1}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ so $\hat{S}_1^2\alpha_1 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2\alpha_1$

Likewise, $\hat{S}_2^2\alpha_2 = \frac{3}{4}\hbar^2\alpha_2$

(i) $\chi_{11}(1,2) = \alpha_1\alpha_2$:

$$\hat{S}_1^2\alpha_1\alpha_2 = \left(\hat{S}_1^2\alpha_1\right)\alpha_2 = \frac{3}{4}\hbar^2\alpha_1\alpha_2$$

$$\hat{S}_2^2\alpha_1\alpha_2 = \alpha_1\left(\hat{S}_2^2\alpha_2\right) = \frac{3}{4}\hbar^2\alpha_1\alpha_2$$

Using the results from Q11: -

$$\hat{S}_{x1}\hat{S}_{x2}\alpha_1\alpha_2 = \hat{S}_{x1}\alpha_1\hat{S}_{x2}\alpha_2 = \frac{\hbar}{2}\beta_1\frac{\hbar}{2}\beta_2 = \frac{\hbar^2}{4}\beta_1\beta_2$$

$$\hat{S}_{y1}\hat{S}_{y2}\alpha_1\alpha_2 = \hat{S}_{y1}\alpha_1\hat{S}_{y2}\alpha_2 = i\frac{\hbar}{2}\beta_1 i\frac{\hbar}{2}\beta_2 = -\frac{\hbar^2}{4}\beta_1\beta_2$$

$$\hat{S}_{z1}\hat{S}_{z2}\alpha_1\alpha_2 = \hat{S}_{z1}\alpha_1\hat{S}_{z2}\alpha_2 = \frac{\hbar}{2}\alpha_1\frac{\hbar}{2}\alpha_2 = \frac{\hbar^2}{4}\alpha_1\alpha_2$$

Hence

$$\begin{aligned}\hat{S}^2\alpha_1\alpha_2 &= \frac{3}{4}\hbar^2\alpha_1\alpha_2 + \frac{3}{4}\hbar^2\alpha_1\alpha_2 + 2\left(\frac{\hbar^2}{4}\beta_1\beta_2 - \frac{\hbar^2}{4}\beta_1\beta_2 + \frac{\hbar^2}{4}\alpha_1\alpha_2\right)\\ &= 2\hbar^2\alpha_1\alpha_2 = S(S+1)\hbar^2\alpha_1\alpha_2 \quad \text{so} \quad S = 1\end{aligned}$$

$$\begin{aligned}\hat{S}_z\alpha_1\alpha_2 &= \left(\hat{S}_{1z}\alpha_1\right)\alpha_2 + \alpha_1\left(\hat{S}_{2z}\alpha_2\right) = \left(\frac{\hbar}{2}+\frac{\hbar}{2}\right)\alpha_1\alpha_2\\ &= \hbar\alpha_1\alpha_2 = M_S\alpha_1\alpha_2 \quad \text{so} \quad M_S = 1\end{aligned}$$

(ii) Similarly, for $\chi_{1-1}(1,2) = \beta_1\beta_2$

$$\begin{aligned}\hat{S}^2\beta_1\beta_2 &= \frac{3}{4}\hbar^2\beta_1\beta_2 + \frac{3}{4}\hbar^2\beta_1\beta_2 + 2\left(\frac{\hbar^2}{4}\alpha_1\alpha_2 - \frac{\hbar^2}{4}\alpha_1\alpha_2 + \frac{\hbar^2}{4}\beta_1\beta_2\right)\\ &= 2\hbar^2\beta_1\beta_2 = S(S+1)\hbar^2\beta_1\beta_2 \quad \text{so} \quad S = 1\end{aligned}$$

$$\begin{aligned}\hat{S}_z\beta_1\beta_2 &= \left(\hat{S}_{1z}\beta_1\right)\beta_2 + \beta_1\left(\hat{S}_{2z}\beta_2\right) = \left(-\frac{\hbar}{2}-\frac{\hbar}{2}\right)\beta_1\beta_2\\ &= -\hbar\beta_1\beta_2 = M_S\beta_1\beta_2 \quad \text{so} \quad M_S = -1\end{aligned}$$

(iii) For $\chi_{10}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 + \alpha_2\beta_1]$,

$$\hat{S}_1^2\chi_{10}(1,2) = \frac{1}{\sqrt{2}}\left[\left(\hat{S}_1^2\alpha_1\right)\beta_2 + \alpha_2\left(\hat{S}_1^2\beta_1\right)\right] = \frac{1}{\sqrt{2}}\frac{3\hbar^2}{4}[\alpha_1\beta_2 + \alpha_2\beta_1] = \frac{3\hbar^2}{4}\chi_{10}(1,2)$$

$$\hat{S}_2^2\chi_{10}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_1\left(\hat{S}_2^2\beta_2\right) + \left(\hat{S}_2^2\alpha_2\right)\beta_1\right] = \frac{1}{\sqrt{2}}\frac{3\hbar^2}{4}[\alpha_1\beta_2 + \alpha_2\beta_1] = \frac{3\hbar^2}{4}\chi_{10}(1,2)$$

Using the results from Q11: -

$$\hat{S}_{x1}\hat{S}_{x2}\chi_{10}(1,2) = \frac{1}{\sqrt{2}}\left[\left(\hat{S}_{x1}\alpha_1\right)\left(\hat{S}_{x2}\beta_2\right) + \left(\hat{S}_{x2}\alpha_2\right)\left(\hat{S}_{x1}\beta_1\right)\right] = \frac{1}{\sqrt{2}}\frac{\hbar^2}{4}[\beta_1\alpha_2 + \beta_2\alpha_1] = \frac{\hbar^2}{4}\chi_{10}(1,2)$$

$$\hat{S}_{y1}\hat{S}_{y2}\chi_{10}(1,2) = \frac{1}{\sqrt{2}}\left[\left(\hat{S}_{y1}\alpha_1\right)\left(\hat{S}_{y2}\beta_2\right) + \left(\hat{S}_{y2}\alpha_2\right)\left(\hat{S}_{y1}\beta_1\right)\right] = \frac{1}{\sqrt{2}}\frac{\hbar^2}{4}[\beta_1\alpha_2 + \beta_2\alpha_1] = \frac{\hbar^2}{4}\chi_{10}(1,2)$$

$$\hat{S}_{y1}\hat{S}_{y2}\chi_{10}(1,2)=\frac{1}{\sqrt{2}}\left[\left(\hat{S}_{z1}\alpha_1\right)\left(\hat{S}_{z2}\beta_2\right)+\left(\hat{S}_{z2}\alpha_2\right)\left(\hat{S}_{z1}\beta_1\right)\right]=\frac{1}{\sqrt{2}}\frac{\hbar^2}{4}\left[-\alpha_1\beta_2-\alpha_2\beta_1\right]=-\frac{\hbar^2}{4}\chi_{10}(1,2)$$

Hence

$$\hat{S}^2\chi_{10}(1,2)=\left[\frac{3\hbar^2}{4}+\frac{3\hbar^2}{4}+2\left(\frac{\hbar^2}{4}+\frac{\hbar^2}{4}-\frac{\hbar^2}{4}\right)\right]\chi_{10}(1,2)$$
$$=2\hbar^2\chi_{10}(1,2)=S(S+1)\hbar^2\chi_{10}(1,2)\quad \text{so}\quad S=1$$

$$\hat{S}_z\chi_{10}(1,2)=\left(\hat{S}_{z1}+\hat{S}_{z2}\right)\chi_{10}(1,2)=\frac{1}{\sqrt{2}}\left[\left(\hat{S}_{z1}\alpha_1\right)\beta_2+\alpha_2\left(\hat{S}_{z1}\beta_1\right)\right]+\frac{1}{\sqrt{2}}\left[\alpha_1\left(\hat{S}_{z2}\beta_2\right)+\left(\hat{S}_{z2}\alpha_2\right)\beta_1\right]$$
$$=\frac{1}{\sqrt{2}}\frac{\hbar}{2}\left[\alpha_1\beta_2-\alpha_2\beta_1-\alpha_1\beta_2+\alpha_2\beta_1\right]=\left(\frac{\hbar}{2}-\frac{\hbar}{2}\right)\chi_{10}(1,2)=M_S\chi_{10}(1,2)\quad \text{so}\quad M_S=0$$

(iv) Similarly, for $\chi_{00}(1,2)=\frac{1}{\sqrt{2}}\left[\alpha_1\beta_2-\alpha_2\beta_1\right]$,

$$\hat{S}^2\chi_{00}(1,2)=\left[\frac{3\hbar^2}{4}+\frac{3\hbar^2}{4}+2\left(-\frac{\hbar^2}{4}-\frac{\hbar^2}{4}-\frac{\hbar^2}{4}\right)\right]\chi_{00}(1,2)$$
$$=0\chi_{00}(1,2)=S(S+1)\hbar^2\chi_{00}(1,2)\quad \text{so}\quad S=0$$

$$\hat{S}_z\chi_{00}(1,2)=\left(\hat{S}_{z1}+\hat{S}_{z2}\right)\chi_{00}(1,2)=\frac{1}{\sqrt{2}}\left[\left(\hat{S}_{z1}\alpha_1\right)\beta_2-\alpha_2\left(\hat{S}_{z1}\beta_1\right)\right]+\frac{1}{\sqrt{2}}\left[\alpha_1\left(\hat{S}_{z2}\beta_2\right)-\left(\hat{S}_{z2}\alpha_2\right)\beta_1\right]$$
$$=\frac{1}{\sqrt{2}}\frac{\hbar}{2}\left[\alpha_1\beta_2+\alpha_2\beta_1-\alpha_1\beta_2-\alpha_2\beta_1\right]=\left(\frac{\hbar}{2}-\frac{\hbar}{2}\right)\chi_{00}(1,2)=M_S\chi_{00}(1,2)\quad \text{so}\quad M_S=0$$

13. The ladder operators are given by

$$\hat{S}_{\pm i}=\hat{S}_{xi}\pm i\hat{S}_{yi}=\frac{\hbar}{2}\left[\begin{pmatrix}0&1\\1&0\end{pmatrix}\pm i\begin{pmatrix}0&-i\\i&0\end{pmatrix}\right]=\frac{\hbar}{2}\left[\begin{pmatrix}0&1\\1&0\end{pmatrix}\pm\begin{pmatrix}0&1\\-1&0\end{pmatrix}\right]$$

So $\hat{S}_{+i}=\hbar\begin{pmatrix}0&1\\0&0\end{pmatrix}$ and $\hat{S}_{-i}=\hbar\begin{pmatrix}0&0\\1&0\end{pmatrix}$

For the single-particle spin state α_i

$$\hat{S}_{+i}\alpha_i=\hbar\begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\hbar\begin{pmatrix}0\\0\end{pmatrix}=0,$$ as required (at the top of the ladder)

and

$$\hat{S}_{-i}\alpha_i = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \hbar\begin{pmatrix}0\\1\end{pmatrix} \propto \beta_i \text{, as required.}$$

For the two-particle spin state $\chi_{11}(1,2)$

$$\hat{S}_{+}\chi_{11}(1,2) = \left(\hat{S}_{+1} + \hat{S}_{+2}\right)\alpha_1\alpha_2 = \left(\hat{S}_{+1}\alpha_1\right)\alpha_2 + \alpha_1\left(\hat{S}_{+2}\alpha_2\right) = 0 \text{, as required.}$$

$$\hat{S}_{-}\chi_{11}(1,2) = \left(\hat{S}_{-1} + \hat{S}_{-2}\right)\alpha_1\alpha_2 = \left(\hat{S}_{-1}\alpha_1\right)\alpha_2 + \alpha_1\left(\hat{S}_{-2}\alpha_2\right) = \hbar\left(\beta_1\alpha_2 + \alpha_1\beta_2\right) \propto \chi_{10}(1,2),$$

as required ($M_S = 0$ is the next rung on the ladder of M_S values when $S = 1$.)

<u>Note:</u>

$$\chi_{10}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_1\beta_2 + \alpha_2\beta_1\right]$$

and

$$\hat{S}_{-i}\beta_i = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \hbar\begin{pmatrix}0\\0\end{pmatrix} = 0$$

So

$$\begin{aligned}\hat{S}_{-}\chi_{10}(1,2) &= \frac{1}{\sqrt{2}}\left[\left(\hat{S}_{-1}\alpha_1\right)\beta_2 + \alpha_2\left(\hat{S}_{-1}\beta_1\right) + \alpha_1\left(\hat{S}_{-2}\beta_2\right) + \left(\hat{S}_{-2}\alpha_2\right)\beta_1\right]\\ &= \frac{1}{\sqrt{2}}\left[\hbar\beta_1\beta_2 + 0 + 0 + \hbar\beta_1\beta_2\right] = \frac{2\hbar}{\sqrt{2}}\left(\beta_1\beta_2\right) \propto \chi_{1-1}(1,2)\end{aligned}$$

` as required.