Tutorial 4: Solutions

1. Average distance between two indistinguishable particles

(a) Distinguishable particles.

$$|\psi\rangle = |\psi_a\rangle \otimes |\psi_b\rangle$$

where $|\psi\rangle$ is the two-particle ket in the Hilbert space $\mathcal{V}_1 \otimes \mathcal{V}_2$ ($\mathcal{V}_1$ is the Hilbert space for particle 1 and $\mathcal{V}_2$ is the Hilbert space for particle 2).

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 + x_2^2 - 2x_1x_2 \rangle$$

$$\begin{aligned}\langle x_1^2 \rangle &= \langle \psi | x_1^2 \otimes \mathbf{1}_2 | \psi \rangle \\ &= \langle \psi_a | x_1^2 | \psi_a \rangle \langle \psi_b | \mathbf{1} | \psi_b \rangle \\ &= \langle x^2 \rangle_a\end{aligned}$$

(Comment: The subscript 1 in x_1^2 tells us that $\hat{x_1}^2$ is operating in $\mathcal{V}_1$. We can also consider the following:

$$\begin{aligned}\langle x_1, x_2 | \psi \rangle &= \langle x_1 | \psi_a \rangle \langle x_2 | \psi_b \rangle \\ \psi(x_1, x_2) &= \psi_a(x_1)\psi_b(x_2) \\ \langle \psi | x_1^2 | \psi \rangle &= \int dx_1 \int dx_2 \psi_a^*(x_1)\psi_b^*(x_2) x_1^2 \psi_a(x_1)\psi_b(x_2) \\ &= \int dx_1 \psi_a^*(x_1) x_1^2 \psi_a(x_1) \\ &= \langle x^2 \rangle_a\end{aligned}$$
)

Similarly,

$$\begin{aligned}\langle x_2^2 \rangle &= \langle \psi | \mathbf{1}_1 \otimes x_2^2 | \psi \rangle \\ &= \langle \psi_a | \mathbf{1} | \psi_a \rangle \langle \psi_b | x_2^2 | \psi_b \rangle \\ &= \langle x^2 \rangle_b \\ \langle \psi | x_1 x_2 | \psi \rangle &= \langle \psi_a | x_1 | \psi_a \rangle \langle \psi_b | x_2 | \psi_b \rangle \\ &= \langle x \rangle_a \langle x \rangle_b.\end{aligned}$$

So

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$$

(b)

$$|\phi\rangle_\pm = \frac{1}{\sqrt{2}} \left(|\psi_a\rangle|\psi_b\rangle \pm |\psi_b\rangle|\psi_a\rangle \right)$$

$$\begin{aligned}
\langle x_1^2 \rangle &= \langle \phi | x_1^2 | \phi \rangle \\
&= \frac{1}{2}\Big(\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 \\
&\quad + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \\
&\quad \pm \int x_1^2 \psi_a^*(x_1)\psi_b(x_1) dx_1 \int \psi_b^*(x_2)\psi_a(x_2) dx_2 \\
&\quad \pm \int x_1^2 \psi_b^*(x_1)\psi_a(x_1) dx_1 \int \psi_a^*(x_2)\psi_b(x_2) dx_2 \Big) \\
&= \frac{1}{2}(\langle x^2 \rangle_a + \langle x^2 \rangle_b) \quad \text{by orthonormality of } |\psi_a\rangle \text{ and } |\psi_b\rangle.
\end{aligned}$$

or

$$\begin{aligned}
\langle x_1^2 \rangle &= \langle \phi | x_1^2 | \phi \rangle \\
&= \frac{1}{2}(\langle \psi_a|\langle \psi_b| \pm \langle \psi_b|\langle \psi_a|) x_1^2 (|\psi_a\rangle|\psi_b\rangle \pm |\psi_b\rangle|\psi_a\rangle) \\
&= \frac{1}{2}(\langle \psi_a|x_1^2|\psi_a\rangle\langle \psi_b|\psi_b\rangle + \langle \psi_b|x_1^2|\psi_b\rangle\langle \psi_a|\psi_a\rangle \\
&\quad \pm \langle \psi_a|x_1^2|\psi_b\rangle\langle \psi_b|\psi_a\rangle \pm \langle \psi_b|x_1^2|\psi_a\rangle\langle \psi_a|\psi_b\rangle) \\
&= \frac{1}{2}(\langle x^2 \rangle_a + \langle x^2 \rangle_b)
\end{aligned}$$

Similarly, $\langle x_2^2 \rangle = \frac{1}{2}(\langle x^2 \rangle_a + \langle x^2 \rangle_b)$

$$\begin{aligned}
\langle x_1 x_2 \rangle &= \langle \phi | x_1 x_2 | \phi \rangle \\
&= \frac{1}{2}(\langle \psi_a|\langle \psi_b| \pm \langle \psi_b|\langle \psi_a|) x_1 x_2 (|\psi_a\rangle|\psi_b\rangle \pm |\psi_b\rangle|\psi_a\rangle) \\
&= \frac{1}{2}(\langle \psi_a|x_1|\psi_a\rangle\langle \psi_b|x_2|\psi_b\rangle + \langle \psi_b|x_1|\psi_b\rangle\langle \psi_a|x_2|\psi_a\rangle \\
&\quad \pm \langle \psi_a|x_1|\psi_b\rangle\langle \psi_b|x_2|\psi_a\rangle \pm \langle \psi_b|x_1|\psi_a\rangle\langle \psi_a|x_2|\psi_b\rangle) \\
&= \frac{1}{2}(\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm 2|\langle x \rangle_{ab}|^2) \\
&= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2
\end{aligned}$$

So

$$\begin{aligned}\langle (x_1 - x_2)^2 \rangle_{\pm} &= \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2 \\ &= \langle (x_1 - x_2)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2\end{aligned}$$

(c) For a two-electron system, the singlet state has a symmetric real space wavefunction and the triplet state has an antisymmetric real space wavefunction.

Since $2|\langle x \rangle_{ab}|^2 \geq 0$, 1(b) shows that $\langle (x_1 - x_2)^2 \rangle_+ \leq \langle (x_1 - x_2)^2 \rangle_-$.
In the He atom, the two electrons want to minimize Coulomb repulsion. Therefore a larger $\langle (x_1 - x_2)^2 \rangle$ is favoured. Thus, the antisymmetric real-space wavefunction $|\phi\rangle_-$ is favoured, meaning the triplet state is more stable.
(Comment: Note that the triplet state is known as orthohelium and the singlet state is known as parahelium.)
(Note: As spin-orbit-coupling is small for helium (small $Z = 2$), the total wavefunction for the two electrons is separable into a spin part and a spatial part.)

2. Dimensions of symmetric and antisymmetric subspaces

The Hilbert space of 2 particles can be denoted by $\mathcal{E}_1 \otimes \mathcal{E}_2$. For 2 identical particles, $\mathcal{E}_1 = \mathcal{E}_2 \implies \mathcal{E}_1 \otimes \mathcal{E}_2$ or $\mathcal{E}^{\otimes 2}$.
For N identical particles, $\mathcal{E}^{\otimes N}$. But with symmetrization constraint, dimension of Hilbert space is greatly reduced.
(a) For bosons, e.g., photons, the basis is $\{|H\rangle, |V\rangle\}$.
For 3 photons, the basis consists of

$$\begin{gathered}|HHH\rangle \\ \frac{1}{\sqrt{3}}(|HHV\rangle + |HVH\rangle + |VHH\rangle) \\ \frac{1}{\sqrt{3}}(|VHV\rangle + |HVV\rangle + |VVH\rangle) \\ |VVV\rangle.\end{gathered}$$

(b) The dimension of this symmetric subspace is 4.
(c) For fermions, e.g., electrons occupying the same position. For 2 electrons,

$$|\Psi\rangle = |\phi\rangle \otimes |\chi\rangle$$

$|\phi\rangle$ is symmetric spatial part, $|\chi\rangle$ is antisymmetric spin part, so that $|\Psi\rangle$ is antisymmetric.
For $1e^-$, $\{|\uparrow\rangle, |\downarrow\rangle\}$.
For $2e^-$, $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$.
Due to the antisymmetric constraint,

$$|\chi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

The dimension is 1.
(d) For $3e^-$, according to recipe,

$$|\Psi\rangle \propto \begin{vmatrix} |\phi\rangle_A & |\phi\rangle_B & |\phi\rangle_C \\ |\chi\rangle_A & |\chi\rangle_B & |\chi\rangle_C \\ |\omega\rangle_A & |\omega\rangle_B & |\omega\rangle_C \end{vmatrix}$$

By $\{|\uparrow\rangle, |\downarrow\rangle\}$ for $1e^-$,

$$|\Psi\rangle \propto \begin{vmatrix} |\uparrow\rangle_A & |\uparrow\rangle_B & |\uparrow\rangle_C \\ |\downarrow\rangle_A & |\downarrow\rangle_B & |\downarrow\rangle_C \\ ? & ? & ? \end{vmatrix},$$

which is not a square matrix. The determinant does not exist.
The dimension is 0. Alternatively, by Pauli exclusion principle, $|\underbrace{\uparrow_A \uparrow_B}_{\text{not possible}} \downarrow_C\rangle$ can not exist, so the dimension is 0.

3. Variational principle applied to ground state of He atom

(a)

$$H = \left[\frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)\right] + \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right) \tag{1}$$

$$\langle H\rangle = \left\langle \frac{\vec{p}_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_1}\right\rangle + \left\langle \frac{\vec{p}_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_2}\right\rangle \tag{2}$$

$$+ \frac{(Z-2)e^2}{4\pi\epsilon_0}\left(\left\langle\frac{1}{r_1}\right\rangle_Z + \left\langle\frac{1}{r_2}\right\rangle_Z\right) + \langle V_{ee}\rangle_Z \tag{3}$$

$$= 2Z^2 E_{100} + 2(Z-2)\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle_Z + \langle V_{ee}\rangle_Z \tag{4}$$

$$\langle V_{ee}\rangle_Z = \frac{e^2}{4\pi\epsilon_0}\int\int\Big(\frac{1}{\pi(a/Z)^3}\Big)^2 e^{-2Z(r_1+r_2)/a}\frac{1}{|\vec{r}_1-\vec{r}_2|}\,d^3r_1\,d^3r_2 \tag{5}$$

$$= \frac{e^2}{4\pi\epsilon_0}\Big(\frac{Z^3}{\pi a^3}\Big)^2\int e^{-2Zr_1/a} I_2\,d^3r_1 \tag{6}$$

$$= \frac{e^2}{4\pi\epsilon_0}\Big(\frac{Z^3}{\pi a^3}\Big)^2\int e^{-2Zr_1/a}\frac{\pi a^3}{Z^3 r_1}\Big[1-\Big(1+\frac{Zr_1}{a}\Big)e^{-2Zr_1/a}\Big]\,d^3r_1 \tag{7}$$

$$= \frac{e^2}{4\pi\epsilon_0}\frac{Z^3}{\pi a^3}\int_0^\infty \frac{e^{-2Zr_1/a}}{r_1}\Big[1-\Big(1+\frac{Zr_1}{a}\Big)e^{-2Zr_1/a}\Big](4\pi r_1^2)\,dr_1 \tag{8}$$

$$\text{where }\int f(r)\,d^3r = \int_0^\infty f(r)4\pi r^2\,dr \tag{9}$$

$$\text{when } f(r) \text{ depends on } |\vec{r}| \text{ only.} \tag{10}$$

$$= \frac{e^2}{\epsilon_0}\frac{Z^3}{\pi a^3}\int_0^\infty r_1 e^{-2Zr_1/a}\Big[1-\Big(1+\frac{Zr_1}{a}\Big)e^{-2Zr_1/a}\Big]\,dr_1 \tag{11}$$

$$= \frac{e^2}{\epsilon_0}\frac{Z^3}{\pi a^3}\int_0^\infty r_1 e^{-2Zr_1/a} - r_1 e^{-4Zr_1/a} - \frac{Z}{a}r_1^2 e^{-4Zr_1/a}\,dr_1 \tag{12}$$

To evaluate the integrals, we consider

$$J_n = \int_0^\infty r^n e^{-\alpha r}\,dr\ ,\ \alpha > 0$$

and perform integration by parts.

$$\begin{aligned}
J_n &= \int_0^\infty r^n e^{-\alpha r}\,dr \\
&= \Big[r^n\frac{e^{-\alpha r}}{-\alpha}\Big]_0^\infty - \int_0^\infty n r^{n-1}\frac{e^{-\alpha r}}{-\alpha}\,dr \\
&= 0 + \frac{n}{\alpha}J_{n-1}\ (\text{as } r\to\infty, e^{-\alpha r}\to 0 \text{ faster than } r^n\to\infty) \\
&= \frac{n}{\alpha}J_{n-1} \\
J_0 &= \int_0^\infty e^{-\alpha r}\,dr = \Big[\frac{e^{-\alpha r}}{-\alpha}\Big]_0^\infty = \frac{1}{\alpha} \\
\text{So } J_1 &= \frac{1}{\alpha^2} \\
J_2 &= \frac{2}{\alpha^3}
\end{aligned}$$

This gives:

$$\int_0^\infty r_1 e^{-2Zr_1/a}\,dr_1 = \frac{a^2}{4Z^2} \tag{13}$$

$$\int_0^\infty -r_1 e^{-4Zr_1/a}\,dr_1 = -\frac{a^2}{16Z^2} \tag{14}$$

$$\int_0^\infty -\frac{Z}{a}r_1^2 e^{-4Zr_1/a}\,dr_1 = -\frac{a^2}{32Z^2} \tag{15}$$

$$\langle V_{ee} \rangle_Z = \frac{e^2}{4\pi\epsilon_0}\frac{Z^3}{\pi a^3}4\pi\frac{5a^2}{32Z^2} \tag{16}$$
$$= \frac{5Z}{8a}\frac{e^2}{4\pi\epsilon_0} \tag{17}$$
$$= -\frac{5}{4}ZE_{100} \tag{18}$$

Therefore we arrive at

$$\langle H \rangle = 2Z^2E_{100} + 2(Z-2)\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle_Z - \frac{5}{4}ZE_{100} \tag{19}$$

(b) To obtain the optimal value of Z, we minimize $\langle H \rangle$ with respect to Z:

$$\begin{aligned}
\langle H \rangle &= 2Z^2E_{100} + 2(Z-2)\frac{e^2}{4\pi\epsilon_0}\frac{Z}{a} - \frac{5}{4}ZE_{100} \\
&= 2Z^2E_{100} - \underbrace{4Z(Z-2)E_{100}}_{\text{using } E_{100}=-\frac{e^2}{2(4\pi\epsilon_0)a}} - \frac{5}{4}ZE_{100} \\
&= E_{100}(2Z^2 - 4Z^2 + 8Z - \frac{5}{4}Z) \\
&= E_{100}\Big(-2Z^2 + \frac{27}{4}Z\Big) \\
\frac{d\langle H \rangle}{dZ} &= 0 \Rightarrow -4Z + \frac{27}{4} = 0 \\
&\Rightarrow Z = \frac{27}{16} \\
\frac{d^2\langle H \rangle}{dZ^2} &= -4E_{100} > 0 \Rightarrow \text{minimum point.}
\end{aligned}$$

So optimal $Z = \frac{27}{16} \approx 1.69$.
Substituting $Z \approx 1.69$ in $\langle H \rangle$ gives the ground state energy to be -77.5 eV, which gives a percentage error of about 2% when compared with the experimental ground state energy of -79 eV.

(c) The trial wavefunction does not consider the anti-symmetry of the two-particle wavefunction, and thus does not account for the exchange energy. Since there are parallel spins for the Fe atom, we expect that using the same trial wavefunction would not work well as the exchange energy is not taken into account. For the He atom, there are no parallel spins in the ground state and as such the exchange energy is zero. (The two electrons in He are in a singlet state, which has a symmetric spatial part of the wavefunction.)