

Homework 4

Review class notes and Chapters 6.2, 9 and 10 from the book.
The homework is due in class on Tuesday April 5th.

1. Problems 9.2, 9.3, 9.8, 9.24, 10.5, 10.7 (see 10.6 for definitions), 10.8, 10.9, 10.10

9.2
$$\frac{-\hbar^2}{2m_e r^2} \frac{d}{dr} \left[r^2 \frac{dR(r)}{dr} \right] + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] R(r) = ER(r) ; R(r) = \left(\frac{r}{a_0}\right) e^{-r/2a_0}$$

 $l=1$

$$\frac{-\hbar^2}{2m_e r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} \left(\frac{r}{a_0} e^{-r/2a_0} \right) \right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{r}{a_0} e^{-r/2a_0}$$

$$\frac{-\hbar^2}{2m_e r^2} \frac{d}{dr} \left[\frac{r^2}{a_0} e^{-r/2a_0} - \frac{r^3}{2a_0^2} e^{-r/2a_0} \right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{r}{a_0} e^{-r/2a_0}$$

$$\frac{-\hbar^2}{2m_e r^2} \left[-2 \frac{r^2}{a_0^2} e^{-r/2a_0} + \frac{r^3}{4a_0^3} e^{-r/2a_0} + 2 \frac{r}{a_0} e^{-r/2a_0} \right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{r}{a_0} e^{-r/2a_0}$$

$$\frac{-\hbar^2}{2m_e r^2} \left[-\frac{2r^2}{a_0^2} e^{-r/2a_0} + \frac{r^3}{4a_0^3} e^{-r/2a_0} \right] - \frac{e^2}{4\pi\epsilon_0 a_0} e^{-r/2a_0}$$

$$a_0 = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2}$$

$$\frac{-\hbar^2}{2m_e r^2} \left[-\frac{2r^2 \pi m_e e^2}{a_0 \epsilon_0 \hbar^2} e^{-r/2a_0} + \frac{r^3}{4a_0^3} e^{-r/2a_0} \right] - \frac{e^2}{4\pi\epsilon_0 a_0} e^{-r/2a_0}$$

$$\frac{-\hbar^2}{2m_e r^2} \frac{r^3}{4a_0^3} e^{-r/2a_0} + \frac{e^2}{4\pi a_0 \epsilon_0} e^{-r/2a_0} - \frac{e^2}{4\pi\epsilon_0 a_0} e^{-r/2a_0}$$

$$= \frac{-\hbar^2}{2m_e r^2} \frac{r^3}{4a_0^3} e^{-r/2a_0} = - \frac{e^2}{32\pi a_0 \epsilon_0} \frac{r}{a_0} e^{-r/2a_0}$$

$$E_n = - \frac{e^2}{8\pi\epsilon_0 a_0 n^2} \quad \therefore \underline{\underline{n = 2}}$$

$$(9.3) \quad \Psi_{320}(r, \theta, \phi) = \frac{1}{81\sqrt{6\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2\theta - 1)$$

\(\therefore\) the negative region is where,

$$3\cos^2\theta < 1 \quad \text{or} \quad \cos^{-1}\theta < \frac{1}{\sqrt{3}}$$

This corresponds to the interval between 0.9553 and 2.186 in radians.

The probability is given by the integral.

$$P = \frac{1}{81^2 6\pi} \left(\frac{1}{a_0}\right)^3 \int_0^{2\pi} d\phi \int_{0.9553}^{2.186} (3\cos^2\theta - 1)^2 \sin\theta d\theta \int_0^{\infty} r^2 \frac{r^4}{a_0^4} e^{-2r/3a_0} dr.$$

$$P = \frac{2}{81^2 6\pi} \left(\frac{1}{a_0}\right)^3 \int_{0.9553}^{2.186} (3\cos^2\theta - 1)^2 \sin\theta d\theta \int_0^{\infty} r^2 \frac{r^4}{a_0^4} e^{-2r/3a_0} dr.$$

$$= \frac{2}{81^2 6\pi} \left(\frac{1}{a_0}\right)^3 \left[\frac{6!}{a_0^4 \times \left(\frac{2}{3a_0}\right)^7} \right] \int_{0.9553}^{2.186} (3\cos^2\theta - 1)^2 \sin\theta d\theta$$

$$= \frac{1}{3 \times 81^2} \left(\frac{1}{a_0}\right)^3 \frac{6! a_0^3 3^7}{2^7} \int_{0.9553}^{2.186} (3\cos^2\theta - 1)^2 \sin\theta d\theta$$

$$= \frac{6! \times 3^7}{3 \times 81^2 \times 2^7} \int_{0.9553}^{2.186} (\sin\theta - 6\cos^2\theta \sin\theta + 9\cos^4\theta \sin\theta) d\theta$$

$$= \frac{6! \times 3^7}{3 \times 81^2 \times 2^7} \left[-\cos\theta + 2\cos^3\theta - \frac{9}{5}\cos^5\theta \right]_{0.9553}^{2.186}$$

$$= \frac{6! \times 3^7}{3 \times 81^2 \times 2^7} \left[2 \times (0.557 - 0.3849 + 0.1157) \right]$$

$$= 0.625 \times 0.5756 = 0.385$$

(9.8)

$$\langle r \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^3 e^{-2r/a_0} dr.$$

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr.$$

Using the standard integral,

$$\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$$

$$\langle r \rangle = \frac{4}{a_0^3} \frac{6a_0^4}{16} = \underline{\underline{\frac{3}{2} a_0}}$$

$$9.24 \quad \psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\begin{aligned} & -\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} \right] - \frac{e^2}{4\pi \epsilon_0 r} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi) \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial e^{-r/a_0}}{\partial r} \right) \right] - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{e^2}{4\pi \epsilon_0 r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} e^{-r/a_0} \left(r^2 \frac{-2r}{a_0^2} - \frac{2r}{a_0} \right) \right] - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{e^2}{4\pi \epsilon_0 r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0} \right) e^{-r/a_0} - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[-\frac{\hbar^2}{\mu a_0} + \frac{e^2}{4\pi \epsilon_0 r} \right] \frac{1}{r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0} \right) e^{-r/a_0} - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[-\frac{\hbar^2 \mu e^2}{\mu \epsilon_0 \hbar^2} + \frac{e^2}{4\pi \epsilon_0 r} \right] \frac{1}{r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0^2} \right) e^{-r/a_0} - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[\frac{-e^2}{4\pi \epsilon_0} + \frac{e^2}{4\pi \epsilon_0} \right] \frac{1}{r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0} \frac{\pi \mu e^2}{4\pi^2 \hbar^2 \epsilon_0} \right) e^{-r/a_0} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{-e^2}{8\pi \epsilon_0 a_0} \right) e^{-r/a_0} \end{aligned}$$

The function is an eigen function of the Schrödinger equation with the eigen value

$$E = \underline{\underline{\frac{-e^2}{8\pi \epsilon_0 a_0}}}$$

10.5

$$(a) |Y_0^0(\theta, \phi)|^2 + |Y_1^0(\theta, \phi)|^2 + |Y_1^{-1}(\theta, \phi)|^2 = \frac{3}{4\pi} \cos^2 \theta + \frac{3}{8\pi} \sin^2 \theta + \frac{3}{8\pi} \sin^2 \theta$$

$$(b) \frac{3}{4\pi} \cos^2 \theta + \frac{3}{8\pi} \sin^2 \theta + \frac{3}{8\pi} \sin^2 \theta = \frac{3}{4\pi} (\cos^2 \theta + \sin^2 \theta) = \frac{3}{4\pi} \quad \text{Not a function of } \theta, \phi.$$

(c). If a function is independent of θ and ϕ , then it has the same value for all θ , and ϕ . This is what is meant by spherical symmetry.

10.7 Solve this problem by acting on $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$, separately and combining the results.

$$\begin{aligned}
 \hat{S}_{\text{total}}^2 \alpha(1)\beta(2) &= \hat{S}_1^2 \alpha(1)\beta(2) + \hat{S}_2^2 \alpha(1)\beta(2) + 2(\hat{S}_{1x}\hat{S}_{2x}\alpha(1)\beta(2) + \hat{S}_{1y}\hat{S}_{2y}\alpha(1)\beta(2) + \hat{S}_{1z}\hat{S}_{2z}\alpha(1)\beta(2)) \\
 &= \beta(2)\hat{S}_1^2 \alpha(1) + \alpha(1)\hat{S}_2^2 \beta(2) + 2(\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\beta(2) + \hat{S}_{1y}\alpha(1)\hat{S}_{2y}\beta(2) + \hat{S}_{1z}\alpha(1)\hat{S}_{2z}\beta(2)) \\
 &= \frac{3\hbar^2}{4}\alpha(1)\beta(2) + \frac{3\hbar^2}{4}\alpha(1)\beta(2) + 2(\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\beta(2) + \hat{S}_{1y}\alpha(1)\hat{S}_{2y}\beta(2) + \hat{S}_{1z}\alpha(1)\hat{S}_{2z}\beta(2)) \\
 &= \frac{3\hbar^2}{4}\alpha(1)\beta(2) + \frac{3\hbar^2}{4}\alpha(1)\beta(2) + 2 \times \frac{\hbar}{2} (\hat{S}_{1x}\alpha(1)\alpha(2) - i\hat{S}_{1y}\alpha(1)\alpha(2) - \hat{S}_{1z}\alpha(1)\beta(2)) \\
 &= \frac{3\hbar^2}{4}\alpha(1)\beta(2) + \frac{3\hbar^2}{4}\alpha(1)\beta(2) + 2 \times \left(\frac{\hbar}{2}\right)^2 (\beta(1)\alpha(2) - i^2\beta(1)\alpha(2) - \alpha(1)\beta(2)) \\
 &= \frac{3\hbar^2}{2}\alpha(1)\beta(2) + \frac{\hbar^2}{2}(2\beta(1)\alpha(2) - \alpha(1)\beta(2)) \\
 &= \hbar^2\alpha(1)\beta(2) + \hbar^2\beta(1)\alpha(2) \quad \text{--- (1)}
 \end{aligned}$$

$$\begin{aligned}
 \hat{S}_{\text{total}}^2 \beta(1)\alpha(2) &= \hat{S}_1^2 \beta(1)\alpha(2) + \hat{S}_2^2 \beta(1)\alpha(2) + 2(\hat{S}_{1x}\hat{S}_{2x}\beta(1)\alpha(2) + \hat{S}_{1y}\hat{S}_{2y}\beta(1)\alpha(2) + \hat{S}_{1z}\hat{S}_{2z}\beta(1)\alpha(2)) \\
 &= \alpha(2)\hat{S}_1^2 \beta(1) + \beta(1)\hat{S}_2^2 \alpha(2) + 2(\hat{S}_{1x}\beta(1)\hat{S}_{2x}\alpha(2) + \hat{S}_{1y}\beta(1)\hat{S}_{2y}\alpha(2) + \hat{S}_{1z}\beta(1)\hat{S}_{2z}\alpha(2)) \\
 &= \frac{3\hbar^2}{4}\beta(1)\alpha(2) + \frac{3\hbar^2}{4}\beta(1)\alpha(2) + 2(\hat{S}_{1x}\beta(1)\hat{S}_{2x}\alpha(2) + \hat{S}_{1y}\beta(1)\hat{S}_{2y}\alpha(2) + \hat{S}_{1z}\beta(1)\hat{S}_{2z}\alpha(2)) \\
 &= \frac{3\hbar^2}{4}\beta(1)\alpha(2) + \frac{3\hbar^2}{4}\beta(1)\alpha(2) + 2 \times \frac{\hbar}{2} (\hat{S}_{1x}\beta(1)\beta(2) + i\hat{S}_{1y}\beta(1)\beta(2) + \hat{S}_{1z}\beta(1)\alpha(2)) \\
 &= \frac{3\hbar^2}{4}\beta(1)\alpha(2) + \frac{3\hbar^2}{4}\beta(1)\alpha(2) + 2 \times \left(\frac{\hbar}{2}\right)^2 (\alpha(1)\beta(2) - i^2\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
 &= \frac{3\hbar^2}{2}\beta(1)\alpha(2) + \frac{\hbar^2}{2}(2\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
 &= \hbar^2\alpha(1)\beta(2) + \hbar^2\beta(1)\alpha(2). \quad \text{--- (2)}
 \end{aligned}$$

$\therefore \hat{S}_{\text{tot}}^2$ acting on $\frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}}$ yields \rightarrow (1) + (2)

$$\begin{aligned}
 &= \frac{1}{\sqrt{2}} \left[\hbar^2\alpha(1)\beta(2) + \hbar^2\beta(1)\alpha(2) + \hbar^2\alpha(1)\beta(2) + \hbar^2\beta(1)\alpha(2) \right] \\
 &= \frac{2\hbar^2}{\sqrt{2}} \left[\alpha(1)\beta(2) + \beta(1)\alpha(2) \right]
 \end{aligned}$$

$\therefore \hat{S}_{\text{total}}^2$ acting on $\frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}}$ is $2\hbar^2$.
 $\Rightarrow \frac{1}{\sqrt{2}} \left[\hbar^2\alpha(1)\beta(2) + \hbar^2\beta(1)\alpha(2) - \hbar^2\alpha(1)\beta(2) - \hbar^2\beta(1)\alpha(2) \right]$
 $= \frac{1}{\sqrt{2}} \times 0 \left[\alpha(1)\beta(2) + \beta(1)\alpha(2) \right]$
 The eigen value is $0 \times \frac{\sqrt{2}}{2} \hbar^2$

10.8

$$\frac{\partial e^{-\alpha r}}{\partial r} = -\alpha e^{-\alpha r}$$

$$\frac{\partial}{\partial r} (-\alpha r^2 e^{-\alpha r}) = -2\alpha r e^{-\alpha r} + \alpha^2 r^2 e^{-\alpha r}$$

$$(a) \hat{H}\Phi = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \left(-2\alpha r e^{-\alpha r} + \alpha^2 r^2 e^{-\alpha r} \right) - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r} = \frac{\alpha\hbar^2}{2m_e r^2} (2r - \alpha r^2) e^{-\alpha r} - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r}$$

$$(b) \int \Phi^* \hat{H} \Phi d\tau = \frac{\alpha\hbar^2}{2m_e} \left[2 \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r e^{-2\alpha r} dr - \alpha \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 e^{-2\alpha r} dr \right] - \frac{e^2}{4\pi\epsilon_0} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r e^{-2\alpha r} dr$$

$$= \frac{4\pi\alpha\hbar^2}{2m_e} \left(2 \int_0^\infty r e^{-2\alpha r} dr - \alpha \int_0^\infty r^2 e^{-2\alpha r} dr \right) - \frac{e^2}{\epsilon_0} \int_0^\infty r e^{-2\alpha r} dr$$

$$= \frac{2\pi\alpha\hbar^2}{m_e} \left(2 \frac{1!}{2^2\alpha^2} - \alpha \frac{2!}{2^3\alpha^3} \right) - \frac{e^2}{\epsilon_0} \frac{1!}{2^2\alpha^2} = \frac{\pi\hbar^2}{2m_e\alpha} - \frac{e^2}{4\epsilon_0\alpha^2}$$

$$(c) \int \Phi^* \Phi d\tau = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 e^{-2\alpha r} dr$$

$$= 4\pi \int_0^\infty r^2 e^{-2\alpha r} dr = 4\pi \frac{2!}{2^3\alpha^3} = \frac{\pi}{\alpha^3}$$

$$(d) \frac{d}{d\alpha} \left(\frac{\hbar^2\alpha^2}{2m_e} - \frac{e^2\alpha}{4\pi\epsilon_0} \right) = -\frac{e^2}{4\pi\epsilon_0} + \frac{\hbar^2\alpha}{m_e} = 0$$

$$\alpha_{\text{optimal}} = \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}$$

$$(e) E(\alpha) = \frac{\hbar^2\alpha^2}{2m_e} - \frac{e^2\alpha}{4\pi\epsilon_0} = \frac{\hbar^2}{2m_e} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right)^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right) = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$$

$E(\alpha_{\text{optimal}})$ is equal to the true energy because our trivial wave function has the same form as the true wave function.

109

The data set shown by the middle curve is correct. Although the alkali atoms have the lowest ionization energies, they must have the highest 2nd ionization energy, as the singly charged positive ions have the rare gas filled shell configuration. The experiments that produced the data set shown by the upper curve had assigned atomic numbers that were too low by one.

10.10

$$(a) [1s(1)2s(2) + 2s(1)1s(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$[1s(2)2s(1) + 2s(2)1s(1)] [\alpha(2)\beta(1) - \beta(2)\alpha(1)] = - [1s(1)2s(2) + 2s(1)1s(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

\therefore The function is antisymmetric in the exchange of electrons ① and ②.

$$(b) [1s(1)2s(2) + 2s(1)1s(2)] \alpha(1)\alpha(2)$$

$$[1s(2)2s(1) + 2s(2)1s(2)] \alpha(2)\alpha(1) = [1s(1)2s(2) + 2s(1)1s(2)] \alpha(1)\alpha(2)$$

\therefore The function is symmetric in the exchange of electrons ① and ②.

$$(c) [1s(1)2s(2) + 1s(2)2s(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$[1s(2)2s(1) + 1s(1)2s(2)] [\alpha(2)\beta(1) + \alpha(1)\beta(2)] = [1s(1)2s(2) + 1s(2)2s(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

\therefore The function is symmetric in the exchange of electrons ① and ②.

$$(d) [1s(1)2s(2) - 1s(2)2s(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$[1s(2)2s(1) - 1s(1)2s(2)] [\alpha(2)\beta(1) + \alpha(1)\beta(2)] = - [1s(1)2s(2) - 1s(2)2s(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

\therefore The function is antisymmetric in the exchange of electrons ① and ②.

$$(e) [1s(1)2s(2) + 1s(2)2s(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1) + \alpha(1)\alpha(2)]$$

$$[1s(2)2s(1) + 1s(1)2s(2)] [\alpha(2)\beta(1) - \alpha(1)\beta(2) + \alpha(2)\alpha(1)]$$

$$\neq \pm [1s(1)2s(2) + 1s(2)2s(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1) + \alpha(1)\alpha(2)]$$

\therefore The function is neither symmetric nor antisymmetric in the exchange of electrons ① and ②.