Problem Set 4

Q20.5 How do the results shown in Figure 20.10 differ from the predictions of the Bohr model of the H atom?

The Bohr model predicts that the electron orbits are on sharply defined spherical shells so that the radial distribution function would show a sharp spike rather than broadened peaks at specific values of $r$.

Q20.9 If the probability density of finding the electron in the 1s orbital in the H atom has a maximum value at $r = 0$, does that mean that the proton and electron are located at the same point in space?

No, the probability is the product of the probability density and the volume over which the probability is being determined. Because the volume of the nucleus is very small, the probability of finding the electron in the volume corresponding to the nucleus is very small.

P20.7 Calculate the expectation value of the radius $<r>$ at which you would find the electron if the H atom wave function is $\psi_{100}(r)$.

\[
<r> = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^3 e^{-2r/a_0} dr = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr
\]

Using the standard integral $\int_0^\infty r^n e^{-ar} dr = \frac{n!}{a^{n+1}}$,

\[
<r> = \frac{4}{a_0^3} \frac{6a_0^3}{16} = \frac{3a_0}{2}
\]

Q21.7 Explain why shielding is more effective by electrons in a shell of lower principal quantum number than by electrons having the same principal quantum number.

Electrons in a shell of lower principal quantum number have a higher probability of being found between the nucleus and outer electrons than do the electrons with the same principal quantum number. Therefore shielding is more effective by electrons in a shell of lower principal quantum number.
P21.8 Use the variational method to find the optimal 1s wave function for the hydrogen atom starting with trial function \( \Phi(r) = \exp(-\alpha r) \) with \( \alpha \) the variational parameter. Minimize with respect to \( \alpha \) the following:

\[
E(\alpha) = \frac{\int \Phi^* \hat{H}\Phi d\tau}{\int \Phi^* \Phi d\tau}
\]

(a) Show \( \hat{H}\Phi = -\hbar^2 \frac{\partial}{\partial r} \left( \frac{r^2 \partial \Phi}{\partial r} \right) - \frac{e^2}{4\pi \varepsilon_0 r} \Phi = \frac{\alpha \hbar^2}{2m_e r^3} (2r - \alpha r^2) e^{-\alpha r} - \frac{e^2}{4\pi \varepsilon_0 r} e^{-\alpha r} \)

Start with \( \frac{\partial e^{-\alpha r}}{\partial r} = -\alpha e^{-\alpha r} \) and \( \frac{\partial(-\alpha r^2 e^{-\alpha r})}{\partial r} = -2\alpha r e^{-\alpha r} + \alpha^2 r^2 e^{-\alpha r} \)

These give \( \hat{H}\Phi = \frac{\alpha \hbar^2}{2m_e r^3} (2r - \alpha r^2) e^{-\alpha r} - \frac{e^2}{4\pi \varepsilon_0 r} e^{-\alpha r} \)

(b) Solve for \( \int \Phi^* \hat{H}\Phi d\tau \)

\[
\int \Phi^* \hat{H}\Phi d\tau = \frac{\alpha \hbar^2}{2m_e} \left( 2 \int d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r e^{-2\alpha r} dr - \alpha \int d\phi \int_0^\pi \int_0^\infty r^2 e^{-2\alpha r} dr \right) - \frac{e^2}{4\pi \varepsilon_0} \int d\phi \int_0^\pi \int_0^\infty r e^{-2\alpha r} dr
\]

\[
\int \Phi^* \hat{H}\Phi d\tau = \frac{4\alpha^2 \hbar^2}{2m_e} - \frac{e^2}{4\alpha^2 \varepsilon_0}
\]

(c) Solve for \( \int \Phi^* \Phi d\tau \)

\[
\int \Phi^* \Phi d\tau = \int d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 e^{-2\alpha r} dr = \frac{\pi}{\alpha}
\]

(d) Minimize \( E(\alpha) \) with respect to \( \alpha \) to find optimal value of \( \alpha \)

\[
\frac{d}{d\alpha} E(\alpha) = \frac{d}{d\alpha} \int \Phi^* \hat{H}\Phi d\tau = \frac{d}{d\alpha} \left( \frac{\alpha \hbar^2}{2m_e} - \frac{e^2 \alpha}{4\pi \varepsilon_0} \right) = \frac{\hbar^2 \alpha}{m_e} - \frac{e^2}{4\pi \varepsilon_0} = 0
\]

Thus \( \alpha_{\text{optimal}} = \frac{m_e e^2}{4\pi \varepsilon_0 \hbar^2} \)

(e) Compare \( E(\alpha_{\text{optimal}}) \) to true energy.

\[
E(\alpha_{\text{optimal}}) = \frac{m_e e^2}{4\pi \varepsilon_0 \hbar^2} = -\frac{m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}
\]
In this case $E(\alpha_{\text{optimal}})$ is equal to the true energy. The reason it is equal to and not greater than the true energy is that the trial function that we chose has the same form as the true wave function.

**P21.10** Classify the following as symmetric, antisymmetric or neither with respect to the exchange of electrons 1 and 2:

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

Switch electrons 1 and 2: $[1s(2)2s(1) + 2s(2)1s(1)][\alpha(2)\beta(1) - \beta(2)\alpha(1)]$

Note that this is $-[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$. Therefore $[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ is antisymmetric with respect to exchange of electrons 1 and 2.

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

(c) $[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ is symmetric, since

Switch electrons 1 and 2: $[1s(2)2s(1) + 2s(2)1s(1)][\alpha(2)\beta(1) + \beta(2)\alpha(1)]$

Note that this is $[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$.

(d) $[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ is antisymmetric, just like (a).

(e) $[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2) + \alpha(1)\alpha(2)]$ is neither $+$ or $-$ original when electrons are switched, therefore it is neither symmetric nor antisymmetric with respect to exchange of electrons 1 and 2.