Physics 624

Quantum Mechanics II

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Homework #5

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1 Problem #1

(i) For a system of three identical bosons residing in different quantum states with quantum numbers f_1, f_2, and f_3 we can use the single particle wave functions $\psi_{fi}(\xi)$ which are normalized to unity to find the wave function of the system. We note that the requirement for bosons is that the wave function must be symmetric under exchange of particles. Which simple allows that all permutations of particles in states are positive. This implies that

$$\psi = \frac{1}{\sqrt{6}}\Big(\psi_{f1}(1)\psi_{f2}(2)\psi_{f3}(3) + \psi_{f1}(3)\psi_{f2}(1)\psi_{f3}(2) + \psi_{f1}(2)\psi_{f2}(3)\psi_{f3}(1) \\ + \psi_{f1}(1)\psi_{f2}(3)\psi_{f3}(2) + \psi_{f1}(3)\psi_{f2}(2)\psi_{f3}(1) + \psi_{f1}(2)\psi_{f2}(1)\psi_{f3}(3)\Big)$$

Note the factor of $1/\sqrt{6}$ is due to normalization of the 6 different possible arrangements of particles as each are equally likely.

(ii) The result from part (i) can be applied to the case for fermions except that we must enforce the requirement that under exchange of particles the wave function is antisymmetric. This implies that for even permutations of the particles the wave function remains positive and for odd permutations the wave function becomes negative. This yields the result

$$\psi = \frac{1}{\sqrt{6}}\Big(\psi_{f1}(1)\psi_{f2}(2)\psi_{f3}(3) + \psi_{f1}(3)\psi_{f2}(1)\psi_{f3}(2) + \psi_{f1}(2)\psi_{f2}(3)\psi_{f3}(1) \\ - \psi_{f1}(1)\psi_{f2}(3)\psi_{f3}(2) - \psi_{f1}(3)\psi_{f2}(2)\psi_{f3}(1) - \psi_{f1}(2)\psi_{f2}(1)\psi_{f3}(3)\Big)$$

Note the normalization remains the same.

2 Problem #2

(i) To find thee electron momentum probability distribution for the $2s$ state of a Hydrogen atom we first take the wave function of that state in coordinate representation as

$$\psi_{2s}(r) = \frac{1}{4\sqrt{2\pi a^3}}\left(2 - \frac{r}{a}\right)e^{-r/2a}$$

where a is the *Bohr radius* given as $a = \hbar^2/me^2$. Now we can calculate the wave function in momentum space by

$$\begin{aligned}
\phi_{2s}(p) &= \frac{1}{(2\pi\hbar)^{3/2}}\int \exp\left(i\frac{\mathbf{p}\cdot\mathbf{r}}{\hbar}\right)\psi_{2s}(r)d^3r \\
&= \frac{1}{(4\pi)^2(a\hbar)^{3/2}}\int_0^\infty\int_0^\pi\int_0^{2\pi} \exp\left(i\frac{pr\cos\theta}{\hbar}\right)\left(2-\frac{r}{a}\right)e^{-r/2a}r^2\sin\theta dr d\theta d\phi \\
&= \frac{\hbar}{4\pi(a\hbar)^{3/2}p}\int_0^\infty \sin\left(\frac{pr}{\hbar}\right)\left(2-\frac{r}{a}\right)e^{-r/2a}r dr \\
&= \frac{\hbar}{4\pi(a\hbar)^{3/2}p}64a^3\hbar^3 p\frac{(4a^2p^2-\hbar^2)}{(4a^2p^2+\hbar^2)^3} \\
&= \frac{16\hbar^{5/2}a^{3/2}}{\pi}\frac{(4a^2p^2-\hbar^2)}{(4a^2p^2+\hbar^2)^3}
\end{aligned}$$

So we can find the square of the wave function as the electron momentum probability distribution for the $2s$ state as

$$|\phi_{2s}(p)|^2 = \frac{256\hbar^5a^3}{\pi^2}\frac{(4a^2p^2-\hbar^2)^2}{(4a^2p^2+\hbar^2)^6}$$

(ii) Now for the $2p$ states we take the wave function to be in a superposition of the three possible l states $(l = -1, 0, 1)$

$$\psi_{2p}(r,\theta,\phi) = \frac{1}{\sqrt{3}}\Big(\psi_{211}(r,\theta,\phi) + \psi_{210}(r,\theta,\phi) + \psi_{21-1}(r,\theta,\phi)\Big)$$

where we take each state as equally likely. Note we have the eigenfunctions as

$$\begin{aligned}\psi_{210}(r,\theta) &= \frac{1}{4\sqrt{2\pi a^3}}\frac{r}{a}e^{-r/2a}\cos\theta \\ \psi_{21\pm1}(r,\theta,\phi) &= \frac{1}{8\sqrt{2\pi a^3}}\frac{r}{a}e^{-r/2a}\sin\theta e^{\pm i\phi}\end{aligned}$$

Now we calculate the momentum representation of each of the eigenstates by

$$\begin{aligned}\phi_{210}(p) &= \frac{1}{(2\pi\hbar)^{3/2}}\int \exp\left(i\frac{\mathbf{p}\cdot\mathbf{r}}{\hbar}\right)\psi_{210}(r,\theta)d^3r \\ &= \frac{1}{(4\pi)^2(a\hbar)^{3/2}}\int_0^\infty\int_0^\pi\int_0^{2\pi}\exp\left(i\frac{pr\cos\theta}{\hbar}\right)\frac{r}{a}e^{-r/2a}\cos\theta r^2\sin\theta drd\theta d\phi \\ &= \frac{64ia^{5/2}\hbar^{7/2}}{\pi}\frac{p}{(4a^2p^2+\hbar^2)^3}\end{aligned}$$

and

$$\begin{aligned}\phi_{21\pm1}(p) &= \frac{1}{(2\pi\hbar)^{3/2}}\int \exp\left(i\frac{\mathbf{p}\cdot\mathbf{r}}{\hbar}\right)\psi_{21\pm1}(r,\theta,\phi)d^3r \\ &= \frac{1}{(4\pi)^2(a\hbar)^{3/2}}\int_0^\infty\int_0^\pi\int_0^{2\pi}\exp\left(i\frac{pr\cos\theta}{\hbar}\right)\frac{r}{a}e^{-r/2a}\sin\theta e^{\pm i\phi}r^2\sin\theta drd\theta d\phi \\ &= \pm\frac{3ia^{3/2}\hbar^{7/2}}{\pi}\frac{1}{(\hbar^2+4a^2p^2)^{5/2}}\end{aligned}$$

Which allows us to calculate the probability distribution for the $2p$ state as

$$\begin{aligned}|\phi_{2p}(p)|^2 = \frac{1}{3}\Big(|\phi_{210}|^2 + |\phi_{211}|^2 + |\phi_{21-1}|^2\Big) &= \frac{64^2a^5\hbar^7}{3\pi^2}\frac{p^2}{(4a^2p^2+\hbar^2)^6} + \frac{6a^3\hbar^7}{\pi^2}\frac{1}{(\hbar^2+4a^2p^2)^5} \\ &= \frac{2a^3\hbar^7}{3\pi^2}\left(\frac{2048a^2p^2}{(4a^2p^2+\hbar^2)^6} + \frac{9}{(\hbar^2+4a^2p^2)^5}\right) \\ &= \frac{2a^3\hbar^7}{3\pi^2}\frac{2084a^2p^2+9\hbar^2}{(4a^2p^2+\hbar^2)^6}\end{aligned}$$

3 Problem #3

Consider an artificial helium-like two-electron atom where the Coulomb electron-nucleus interaction potential is replaced by a harmonic potential. This has a Hamiltonian of the form

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{8}\left(r_1^2 + r_2^2\right) + \frac{1}{|r_1 - r_2|}$$

where we are working in atomic units and we take the spring constant to be $k = 1/4$ which has an exact ground state solution as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2(8\pi^{5/2} + 5\pi^3)^{1/2}}\left(1 + \frac{1}{2}|\mathbf{r}_1 - \mathbf{r}_2|\right)\exp\left[-\frac{1}{4}(r_1^2 + r_2^2)\right]$$

where the energy of this state is given as $E = 2\,\text{a.u.}$. Using this we can calculate the electron-electron correlation energy by

$$E_c = E - E_0$$

where we can calculate E_0 by

$$E_0 = \frac{\langle\psi_0|H|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle}$$

Taking ψ_0 as the ground-state wave function of the truncated Hamiltonian

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{8}\left(r_1^2 + r_2^2\right)$$

We can see that

$$\psi_0 = \exp\left[-\frac{1}{4}(r_1^2 + r_2^2)\right]$$

note that we neglect the normalization constant as they will not factor into the solution for E_0. Also we can neglect the integration over the angular component as they too will cancel in the calculation of E_0. So we find that

$$\begin{aligned}
\langle\psi_0|\psi_0\rangle &= \int_0^\infty\int_0^\infty \exp\left[-\frac{1}{4}(r_1^2 + r_2^2)\right]^2 r_1^2 r_2^2 dr_1 dr_2 \\
&= \int_0^\infty\int_0^\infty \exp\left[-\frac{1}{2}(r_1^2 + r_2^2)\right] r_1^2 r_2^2 dr_1 dr_2 \\
&= \sqrt{\frac{\pi}{2}}\int_0^\infty \exp\left[-\frac{1}{2}r_2^2\right] r_2^2 dr_2 \\
&= \frac{\pi}{2}
\end{aligned}$$

Now we see that

$$\langle\psi_0|H|\psi_0\rangle = -\frac{1}{2}\int\psi_0\nabla_1^2\psi_0 dr_{12} - \frac{1}{2}\int\psi_0\nabla_2^2\psi_0 dr_{12} + \frac{1}{8}\int\psi_0\left(r_1^2 + r_2^2\right)\psi_0 dr_{12} + \int\psi_0\frac{1}{|\mathbf{r_1} - \mathbf{r_2}|}\psi_0 dr_{12}$$

Has four integration terms so we calculate each as

$$\begin{aligned}
-\frac{1}{2}\int\psi_0\nabla_1^2\psi_0 dr_1 dr_2 &= -\frac{1}{2}\int_0^\infty\int_0^\infty \exp\left[-\frac{1}{4}(r_1^2 + r_2^2)\right]\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\exp\left[-\frac{1}{4}(r_1^2 + r_2^2)\right]\right) r_1^2 r_2^2 dr_1 dr_2 \\
&= -\frac{1}{8}\int_0^\infty\int_0^\infty \exp\left[-\frac{1}{2}(r_1^2 + r_2^2)\right](r_1^2 - 6) r_1^2 r_2^2 dr_1 dr_2 \\
&= -\frac{1}{8}\left(\frac{3\pi}{2} - 6\frac{\pi}{2}\right) = \frac{3\pi}{16}
\end{aligned}$$

Note due to the symmetry of the ψ_0 the integral with the r_2 Laplacian has the identical result. Next we calculate

$$
\begin{aligned}
\frac{1}{8}\int \psi_0 \left(r_1^2+r_2^2\right)\psi_0 dr_{12} &= \frac{1}{8}\int_0^\infty \int_0^\infty \exp\left[-\frac{1}{2}(r_1^2+r_2^2)\right]\left(r_1^2+r_2^2\right) r_1^2 r_2^2 dr_1 dr_2 \\
&= \frac{1}{8}\sqrt{\frac{\pi}{2}}\int_0^\infty \exp\left[-\frac{1}{2}r_2^2\right]\left(3+r_2^2\right) r_2^2 dr_2 \\
&= \frac{3\pi}{8}
\end{aligned}
$$

Finally for the interaction potential we expand into spherical harmonics where

$$
\frac{1}{|\mathbf{r_1}-\mathbf{r_2}|} = \begin{cases} \dfrac{4\pi}{r_1}\sum_{l,m}\dfrac{1}{2l+1}\left(\dfrac{r_2}{r_1}\right)^l Y_{lm}^*(\theta_1,\varphi_1)Y_{lm}(\theta_2,\varphi_2), & r_1 > r_2 \\[2ex] \dfrac{4\pi}{r_2}\sum_{l,m}\dfrac{1}{2l+1}\left(\dfrac{r_1}{r_2}\right)^l Y_{lm}^*(\theta_1,\varphi_1)Y_{lm}(\theta_2,\varphi_2), & r_2 > r_1 \end{cases}
$$

We note due to the orthogonality of the spherical harmonics and the fact that ψ_0 is in the $m=l=0$ state we can simplify the integral to just

$$
\frac{1}{|\mathbf{r_1}-\mathbf{r_2}|} = \begin{cases} \dfrac{1}{r_1}, & r_1 > r_2 \\[2ex] \dfrac{1}{r_2}, & r_2 > r_1 \end{cases}
$$

So we can calculate the interaction term as

$$
\begin{aligned}
\int \psi_0 \frac{1}{|\mathbf{r_1}-\mathbf{r_2}|}\psi_0 dr_{12} &= \int_0^\infty \exp\left[-\frac{1}{2}r_1^2\right]\left(\int_0^{r_1}\frac{1}{r_1}\exp\left[-\frac{1}{2}r_2^2\right] r_2^2 dr_2 + \int_{r_1}^\infty \frac{1}{r_2}\exp\left[-\frac{1}{2}r_2^2\right] r_2^2 dr_2\right) r_1^2 dr_1 \\
&= \frac{\sqrt{\pi}}{2}
\end{aligned}
$$

So this allows us to calculate E_0 by

$$
E_0 = \frac{\langle\psi_0|H|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} = \frac{2}{\pi}\left(\frac{3\pi}{16}+\frac{3\pi}{16}+\frac{3\pi}{8}+\frac{\sqrt{\pi}}{2}\right) = \frac{3}{2}+\frac{1}{\sqrt{\pi}} \approx 2.0642\,\text{a.u.}
$$

So we can see that the correlation energy is about

$$
E_c \approx -0.0642\,\text{a.u.}
$$