**QM 15-030-710-003 Spring ****
Assignment 9: Identity of Particles, Atom**

**The due date for this assignment is ****.**
Reading assignment: Chapters $IX$ and $X$.

1. In a system of two identical bosons with spin $s = 0$, one is described by the WF $\psi_1(\mathbf{r})$ while the other by $\psi_2(\mathbf{r})$. Both functions are normalized and have definite - and opposite - parities. Find the coordinate distribution function of one particle given that the position of the other is arbitrary (and not fixed). What is the probability that a) one of the particles and b) both particles are in the half-space $z \geq 0$? Compare your result with the circumstance of distinguishable particles.

   *Solution*

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) + \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\}$$

$$dw = \left\{\int |\Psi(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2)|^2 dV_2\right\} dV = \frac{1}{2}\left\{|\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2\right\} dV$$

   Using

$$\int_{z\geq 0} |\psi_{1,2}(\mathbf{r})|^2 dV = \frac{1}{2}\int |\psi_{1,2}(\mathbf{r})|^2 dV = \frac{1}{2}$$

   find

$$W_1(z \geq 0) = \frac{1}{2}$$

   where the position of the other particle is arbitrary. The probability for both particles to be in $z \geq 0$ half-space simultaneously is

$$\begin{aligned}
W_2(z_{1,2} \geq 0) &= \int_{z_1\geq 0}\int_{z_2\geq 0} |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 dV_1 dV_2 \\
&= \frac{1}{2}\int_{z_1\geq 0}\int_{z_2\geq 0} |\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 dV_1 dV_2 \\
&\quad + \frac{1}{2}\int_{z_1\geq 0}\int_{z_2\geq 0} |\psi_1(\mathbf{r}_2)|^2 |\psi_2(\mathbf{r}_1)|^2 dV_1 dV_2 \\
&\quad + \frac{1}{2}\int_{z_1\geq 0}\int_{z_2\geq 0} \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1^*(\mathbf{r}_2)\psi_2^*(\mathbf{r}_1) dV_1 dV_2 \\
&\quad + \frac{1}{2}\int_{z_1\geq 0}\int_{z_2\geq 0} \psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) dV_1 dV_2 \\
&= \int_{z_1\geq 0} |\psi_1(\mathbf{r}_1)|^2 dV_1 \int_{z_2\geq 0} |\psi_2(\mathbf{r}_2)|^2 dV_2 + \int_{z_1\geq 0} \psi_1(\mathbf{r}_1)\psi_2^*(\mathbf{r}_1) dV_1 \int_{z_2\geq 0} \psi_2(\mathbf{r}_2)\psi_1^*(\mathbf{r}_2) dV_2 \\
&= \frac{1}{4} + \left|\int_{z_1\geq 0} \psi_1(\mathbf{r})\psi_2^*(\mathbf{r}) dV\right|^2 > \frac{1}{4}
\end{aligned}$$

2. Solve the problem analogous to the preceding problem for the case of two fermions that are in the same spin state.

   *Solution*

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)\} \chi^\alpha \chi^\beta$$

   whereof

$$W_1(z \geq 0) = \frac{1}{2}$$

   and

$$W_2(z_{1,2} \geq 0) = \frac{1}{4} - \left|\int_{z_1\geq 0} \psi_1(\mathbf{r})\psi_2^*(\mathbf{r}) dV\right|^2 < \frac{1}{4}$$

3. Two identical spin-zero bosons interact via the potential energy $U = k\left(\mathbf{r}_1 - \mathbf{r}_2\right)^2/2$. What is the energy spectrum of the system?

*Solution*

Not taking particle identity into account

$$\begin{aligned} E_N &= \hbar\omega\left(N + \frac{3}{2}\right),\ N = n_1 + n_2 + n_3 \\ \Psi_{n_1,n_2,n_3} &= \psi_{n_1}^{osc}(x)\,\psi_{n_2}^{osc}(y)\,\psi_{n_3}^{osc}(z),\ \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \end{aligned}$$

Identity requires that the WF is symmetrical with respect to interchange of particle coordinates, that is $\mathbf{r} \to -\mathbf{r}$. The latter leads to a factor

$$(-1)^{n_1+n_2+n_3} = (-1)^N$$

so that even $N = 0, 2, 4, \ldots$ are realized while odd $N$ must be excluded.

4. A system consists of three identical particles whose coordinates in the centre of mass frame of reference are $\mathbf{r}_1, \mathbf{r}_2$, and $\mathbf{r}_3$ respectively. How does $\mathbf{r}_1 \cdot \mathbf{r}_2$ transform under the permutation of the 1st and 3rd particles? Symmetrize this quantity with respect to permutation of any two particles in the system.

*Solution*

Denoting $\widehat{P}_{1,3}$ the operator of the coordinate permutation of the 1st and 3rd particles. Since $\mathbf{r}_3 = -\left(\mathbf{r}_1 + \mathbf{r}_2\right)$, then $\widehat{P}_{1,3}\mathbf{r}_1 = \mathbf{r}_3 = -\left(\mathbf{r}_1 + \mathbf{r}_2\right)$ and $\widehat{P}_{1,3}\mathbf{r}_2 = \mathbf{r}_2$, $\widehat{P}_{1,3}\left(\mathbf{r}_1 \cdot \mathbf{r}_2\right) = -\left(\mathbf{r}_1 + \mathbf{r}_2\right) \cdot \mathbf{r}_2$. By the same token, $\widehat{P}_{2,3}\left(\mathbf{r}_1 \cdot \mathbf{r}_2\right) = -\left(\mathbf{r}_1 + \mathbf{r}_2\right) \cdot \mathbf{r}_1$. Symmetrization of $\mathbf{r}_1 \cdot \mathbf{r}_2$ yields

$$-\frac{1}{3}\left(\mathbf{r}_1^2 + \mathbf{r}_2^2 + \mathbf{r}_1 \cdot \mathbf{r}_2\right)$$

For instance,

$$\begin{aligned} \widehat{P}_{1,3}\left\{-\frac{1}{3}\left(\mathbf{r}_1^2 + \mathbf{r}_2^2 + \mathbf{r}_1 \cdot \mathbf{r}_2\right)\right\} &= -\frac{1}{3}\left\{\left(\mathbf{r}_1 + \mathbf{r}_2\right)^2 + \mathbf{r}_2^2 - \left(\mathbf{r}_1 + \mathbf{r}_2\right) \cdot \mathbf{r}_1\right\} \\ &= -\frac{1}{3}\left\{\left(\mathbf{r}_1 + \mathbf{r}_2\right) \cdot \mathbf{r}_2 + \mathbf{r}_2^2\right\} = -\frac{1}{3}\left(\mathbf{r}_1^2 + \mathbf{r}_2^2 + \mathbf{r}_1 \cdot \mathbf{r}_2\right) \end{aligned}$$

5. Consider the hyperfine structure (HFS) of the $s$-states of a hydrogenic atom due to the coupling of the magnetic moments of the electron and the nucleus. The nucleus spin is $I$ and the magnetic moment $\mu_0$ so that $\widehat{\boldsymbol{\mu}} = (\mu_0/I)\,\widehat{\mathbf{I}}$. Estimate the magnitude of the HFS splitting and compare it with the FS splitting.

*Solution*

For HFS

$$\begin{aligned} \overline{\widehat{V}} &= \frac{8\pi e\hbar\mu_0}{3mcI}\left|\psi(0)\right|^2 \widehat{\mathbf{I}} \cdot \widehat{\mathbf{s}} \\ &= \frac{4\pi e\hbar\mu_0}{3mcI}\left|\psi(0)\right|^2 \left[J(J+1) - s(s+1) - I(I+1)\right] \\ &= \frac{4\pi e\hbar\mu_0}{3mcI}\left|\psi(0)\right|^2 \left\{\begin{array}{c} I,\ I = J + 1/2 \\ -(I+1),\ I = J - 1/2 \end{array}\right\} \\ \left|\psi(0)\right|^2 &= \frac{Z^3}{\pi a_0^3} = \frac{Z^3 m^3 e^6}{\pi\hbar^6} \end{aligned}$$

wherof

$$\triangle\, E_{HFS} = \frac{4\pi e\hbar\mu_0}{3mcI}\left|\psi(0)\right|^2 (2I+1) \propto \frac{\mu_0 m^2 e^7}{c\hbar^5}$$

On the other hand (see §72),

$$\triangle\, E_{FS} \propto \frac{e^8 m}{c^2\hbar^4}$$

so that the parametric

$$\frac{\triangle\, E_{FS}}{\triangle\, E_{HFS}} \sim \frac{e\hbar}{cm}/\mu_0 \sim \frac{m}{m_p} \sim 10^{-3}$$

which is the ratio of electron and proton magnetons.

6. Find the energy and the ionization potential of the ground state of a two-electron ion using the variational principal. As a trial function, take the product of hydrogenic functions with an effective charge $Z_{eff}$ which plays the role of the variational parameter. Based on your result, can you draw any conclusion with respect to existence of a stable $H^-$ ion?

   *Solution*

   Using

$$\left(-\frac{1}{2}\triangle - \frac{\alpha}{r}\right)\exp\left(-\alpha r\right) = -\frac{\alpha^2}{2}\exp\left(-\alpha r\right)$$

   and rewriting the Hamiltonian as

$$\begin{aligned}\widehat{H} &= -\frac{1}{2}\left(\triangle_1 + \triangle_2\right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= \left(-\frac{1}{2}\triangle_1 - \frac{Z_{eff}}{r_1}\right) + \left(-\frac{1}{2}\triangle_2 - \frac{Z_{eff}}{r_2}\right) - \left(Z - Z_{eff}\right)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\end{aligned}$$

   and using the trial WF

$$\Psi = \frac{Z_{eff}^3}{\pi}\exp\left[-Z_{eff}\left(r_1 + r_2\right)\right]$$

   and the integrals

$$\int \frac{\exp\left(-2\alpha r\right)}{r} dV = \frac{\pi}{\alpha^2} \text{ and } \int\int \frac{\exp\left[-2\alpha\left(r_1 + r_2\right)\right]}{|\mathbf{r}_1 - \mathbf{r}_2|} dV_1 dV_2 = \frac{5\pi^2}{8\alpha^5}$$

   we find

$$\overline{E}\left(Z_{eff}\right) = Z_{eff}\left(Z_{eff} - 2Z + \frac{5}{8}\right)$$

   and minimizing with respect to $Z_{eff}$, find $Z_{eff} = Z - 5/16$ and

$$E_0 \approx -\left(Z - \frac{5}{16}\right)^2 \text{ and } I = -\frac{Z^2}{2} - E_0 = \frac{Z^2}{2} - \frac{5Z}{8} + \left(\frac{5}{16}\right)^2$$

   Example 1: $He$, $Z = 2$.

$$I_{var} \approx .85 * 27.2eV \approx 23.1eV$$

   Compare this to experimental value

$$I_{exp} \approx 24.5eV$$

   and the first order perturbation theory result

$$I_{pert}^{(1)} \approx 20.4eV$$

   Example 2: $H^-$, $Z = 1$.

$$E_0 \approx -0.47 > -\frac{1}{2}$$

   so it is not possible to assert stability of such ion. However, such ion does exist and the experimental value of its energy is $E_0 \approx -0.527$.

7. Find the normal states of $N$ and $Cl$ atoms.

   *Solution*

   Electron configuration of $N$ is $(1s)^2(2s)^2(2p)^3$ and the normal state is $^4S_{3/2}$ (see p. 254 in LL).

   Electron configuration of $Cl$ is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^5$. Using again problem on p. 254 in LL, find for $p$-states

$$\begin{matrix}(a)\,1, \frac{1}{2} & (b)\,0, \frac{1}{2} & (c)\,-1, \frac{1}{2} \\ (a')\,1, -\frac{1}{2} & (b')\,0, -\frac{1}{2} & (c')\,-1, -\frac{1}{2}\end{matrix}$$

   Possible (non-negative) pairs of $M_L = \sum m$ and $M_S = \sum \sigma$ are as follows:

$$\begin{matrix}\left(a + a' + b + b' + c\right) & 1, \frac{1}{2} \\ \left(a + a' + b + c + c'\right) & 0, \frac{1}{2}\end{matrix}$$

   so that the only possible terms are $^2P_{1/2}$ and $^2P_{3/2}$. Since the shell is more than half full, the normal state is $^2P_{3/2}$.

8. Using the Thomas-Fermi model, find the dependence of the mean distance and mean squared distance of the electron from the nucleus on $Z$. What is $\overline{r^n}$ for $n \geq 3$? - explain your result.

*Solution*

In the Thomas-Fermi model (see eq. (70.9))

$$n(r) = \frac{9Z^2}{9\pi^3}\left[\frac{\chi(x)}{x}\right]^{3/2}, \; x = \frac{rZ^{1/3}}{b}$$

Since $\int n(r)\,dV = Z$, $w(r) = Z^{-1}n(r)$ is the coordinate distribution function for an individual electron. Hence,

$$\begin{aligned} \overline{r^n} &= \int r^n w(r)\,dV = 4\pi Z^{-1}\int r^{n+2}n(r)\,dr = C_n Z^{-n/3} \\ C_n &= b^n \int_0^\infty x^{n+2}\left[\frac{\chi(x)}{x}\right]^{3/2} dx \end{aligned}$$

It follows that

$$\bar{r} \propto Z^{-1/3}$$

and, since $\chi(x) \propto x^{-3}$ at $x \to \infty$, $\overline{r^n} = \infty$ for $n \geq 3$. The latter is because the model predicts too slow a decay at large distances (and, in fact, its applicability is limited to $r \sim 1$; see also footnote on p. 262).

9. Using the Thomas-Fermi model, find the dependence on $Z$ of the typical value of the orbital angular momentum of the electron and of the energy of full ionization of the atom.

*Solution*

Let $\ell$ be the size of the region containing majority of the electrons. From

$$\nabla^2\phi \sim \frac{\phi}{\ell^2} \sim \phi^{3/2}$$

find

$$\phi \sim \ell^{-4}$$

On the other hand,

$$Z \sim n\ell^3 \sim \phi^{3/2}\ell^3 \sim \ell^{-3}$$

so that

$$\ell \sim Z^{-1/3}$$

Angular momentum

$$l \sim \ell p \sim \ell n^{1/3} \sim \ell\phi^{1/2} \sim \ell^{-1} \sim Z^{1/3}$$

Energy

$$\varepsilon \sim p^{2\,\tilde{}}\,\ell^{-4} \sim Z^{4/3}$$

Total energy (and the energy of full ionization)

$$E \sim \varepsilon Z \sim Z^{7/3}$$