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Problem Sheet 3
Further Quantum Mechanics

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Question 1

A system has n non-degenerate single-particle states. These states account for all the degrees of freedom of the particle —— position and (if relevant) spin. The states are occupied by a number p of similar non-interacting particles, without any constraints except for those arising from symmetry under particle exchange. How many distinct many-particle states are there for the p-particle system in the following cases:

(i) if the particles are distinguishable;

(ii) if the particles are identical fermions and $p = n$;

(iii) if the particles are identical bosons and $p = n = 2$;

(iv) if the particles are identical bosons and $p = n = 3$.

✓ *Solution.* (i) If all the particles are distinguishable, then for each particle there are n possible states, The total number of microstates is n^p.

✓ (ii) If the particles are fermions, then by Pauli exclusion principle, each state can be occupied by 0 or 1 fermions only. Since $p = n$, there is a unique microstate, in which every state of the system is occupied by a fermion.

(iii) If the particles are bosons, then each state in the system can be occupied by arbitrarily many particles. We can list the possible microstates as follows:

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$$(2, 0),\ (1, 1),\ (0, 2)$$

where (a, b) indicates that the first state is occupied by a particles and the second state is occupied by b particles.

So there are 3 distinct microstates.

(iv) We can list the possible microstates as follows:

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$$(3, 0, 0),\ (0, 3, 0),\ (0, 0, 3),\ (2, 1, 0),\ (2, 0, 1),\ (1, 2, 0),\ (0, 2, 1),\ (0, 1, 2),\ (1, 0, 2),\ (1, 1, 1)$$

✓ So there are 10 distinct microstates. $\square$

Question 2

Consider two identical, non-interacting particles, each of mass m, with coordinates x_1, x_2. They are confined to a box of length L, so that $0 \leq x_1, x_2 \leq L$.

Suppose the particles are identical spin-zero bosons. What is the wavefunction $\psi(x_1, x_2)$ if the system is in an eigenstate with total energy: (i) $\hbar^2\pi^2/mL^2$, or (ii) $5\hbar^2\pi^2/2mL^2$?

Suppose alternatively that the particles are identical spin-half fermions: for the same values of total energy write down a complete set of possible wavefunctions, as products of space and spin factors.

Solution. First we consider a single particle in the one-dimensional box of length L. It is known that the energy levels of the system are

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$$E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2}$$

and the eigenstates are

$$\langle x|n\rangle = \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{L}\right).$$

Now, since the two particles are non-interacting, by separation of variables, we can reduce the TISE to two independent TISE for each particles, and the energy of the system is simply $E = (E_1)_k + (E_2)_n$.

Suppose that the particles are identical spin-zero bosons.

(i) The energy

$$E = \frac{\hbar^2\pi^2}{mL^2} = \frac{\hbar^2\pi^2k^2}{2mL^2} + \frac{\hbar^2\pi^2n^2}{2mL^2} \implies k^2+n^2=2 \implies (k,n)=(1,1)$$

The eigenstate of $\hat{H}$ is the state $|1\rangle \otimes |1\rangle$. The wave function is:

$$\psi(x_1,x_2) = \psi_1(x_1)\psi_1(x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)$$

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(ii) The energy

$$E = \frac{5\hbar^2\pi^2}{2mL^2} = \frac{\hbar^2\pi^2k^2}{2mL^2} + \frac{\hbar^2\pi^2n^2}{2mL^2} \implies k^2+n^2=5 \implies (k,n)=(1,2) \text{ or } (2,1)$$

The eigenstate of $\hat{H}$ is any linear combinations of $|1\rangle \otimes |2\rangle$ and $|2\rangle \otimes |1\rangle$. But since the particles are bosons, we require that the eigenfunction is symmetric in x_1 and x_2. Then the wave function is given by:

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$$\psi(x_1,x_2) = \frac{1}{\sqrt{2}}(\psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1)) = \frac{\sqrt{2}}{a}\left(\sin\frac{\pi x_1}{L}\sin\frac{2\pi x_2}{L} + \sin\frac{\pi x_2}{L}\sin\frac{2\pi x_1}{L}\right)$$

Suppose that the particles are identical spin-1/2 fermions. In general, the state of the system is the tensor product

$$|\psi\rangle = |\text{space}\rangle \otimes |\text{spin}\rangle$$

~~One of~~ the space factor ~~and~~ the spin factor is symmetric, and the other is anti-symmetric.

(i) The eigenstate of spatial part of $\hat{H}$ is the state $|1\rangle \otimes |1\rangle$. The space factor of the wave function

$$\psi(x_1,x_2) = \psi_1(x_1)\psi_1(x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)$$

is symmetric. So the spin ~~factor is~~ anti-symmetric, which is the singlet state $\frac{1}{\sqrt{2}}(|\uparrow_1\rangle \otimes |\downarrow_2\rangle - |\downarrow_1\rangle \otimes |\uparrow_2\rangle)$. The product state is

$$|\psi\rangle = \frac{1}{\sqrt{2}}|1\rangle \otimes |1\rangle \otimes (|\uparrow_1\rangle \otimes |\downarrow_2\rangle - |\downarrow_1\rangle \otimes |\uparrow_2\rangle) = \frac{1}{\sqrt{2}}|1,1\rangle \otimes (|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle)$$

(ii) The eigenstate ~~of spatial part~~ of $\hat{H}$ ~~is~~ any linear combinations of $|1\rangle \otimes |2\rangle$ and $|2\rangle \otimes |1\rangle$.

If the ~~space factor~~ is symmetric, which is $\frac{1}{\sqrt{2}}|1,2\rangle + |2,1\rangle$, then the spin factor is anti-symmetric. The product state is

$$|\psi_1\rangle = \frac{1}{2}(|1,2\rangle + |2,1\rangle) \otimes (|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle)$$

If the space factor is anti-symmetric, which is $\frac{1}{\sqrt{2}}|1,2\rangle - |2,1\rangle$, then the spin factor is symmetric, which is the triplet states. The product states are:

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}(|1,2\rangle - |2,1\rangle) \otimes |\uparrow_1\uparrow_2\rangle, \quad |\psi_3\rangle = \frac{1}{\sqrt{2}}(|1,2\rangle - |2,1\rangle) \otimes |\downarrow_1\downarrow_2\rangle, \quad |\psi_4\rangle = \frac{1}{2}(|1,2\rangle - |2,1\rangle) \otimes (|\uparrow_1\downarrow_2\rangle + |\downarrow_1\uparrow_2\rangle)$$

The complete set of possible states is $\{|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle, |\psi_4\rangle\}$.

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Question 3. He: ionisation energy.

The ionization energy is the energy required to remove one electron from an atom or ion in its ground state, leaving it in the ground state of the next higher ionization stage. (The energy is often quoted in eV and referred to as an ionization potential.

If we make the (poor) approximation of ignoring the electron-electron repulsion altogether, what value (in eV) is obtained for the ionization potential of the ground state in helium? How much additional energy would then be required to remove the second electron? Assuming these estimates have been made as accurately as reasonably possible within their respective assumptions, state the degree of accuracy of each of these two results (i.e. how close they may be expected to be to the true first and second ionization energies for helium.)

To do better, use the variational method. Using hydrogen-like wavefunctions for both electrons: $\psi_{1s} = \sqrt{Z^3/\pi a_0^3}\exp(-Zr/a_0)$, where Z is an adjustable parameter distinct from the nuclear charge, show that

$$\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle = \frac{2Z}{a_0}$$

Using also $\langle p_1^2 + p_2^2 \rangle = 2Z^2\hbar^2/\left(a_0^2\right)$ and $\langle 1/r_{12} \rangle = 5Z/\left(8a_0\right)$, show that the mean energy as a function of Z is given in terms of the Rydberg R by

$$E(Z) = -2R\left(4Z - Z^2 - 5Z/8\right)$$

Complete the variational procedure, and hence obtain an upper limit for the ground state energy, and a lower limit for the ionization energy of helium.

Solution. If we neglect the electron-electron repulsion, then we can apply separation of variables to the time-independent Schrödinger equation and obtain the same result as for hydrogen-like atoms. The energy levels are

$$E_n = -\frac{Z^2 R}{n^2}$$

✓ where R =13.6 eV. Then the first ionization energy and second ionization energy are both $4R = 54.4$ eV. The estimation for first ionization energy is quite inaccurate. The more precise result which considers electron-electron repulsion is $4 - 2.5)R = 20.4$ eV. The second ionization energy is accurate because He$^+$ is a hydrogen-like ion. ✓

We use the trial wave function $\psi_{1s} = \sqrt{Z^3/\pi a_0^3}\exp(-Zr/a_0)$.

The expectation

$$\left\langle \frac{1}{r} \right\rangle = \iiint_V \frac{Z^3}{\pi a_0^3}\,\mathrm{e}^{-2Zr/a_0}\,\frac{1}{r}\,\mathrm{d}V = \frac{4Z^3}{a_0^3}\int_0^\infty r\,\mathrm{e}^{-2Zr/a_0}\,\mathrm{d}r = \frac{4Z^3}{a_0^3}\left(\frac{a_0}{2Z}\right)^2\Gamma(2) = \frac{Z}{a_0}$$

Then

$$\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle = 2\left\langle \frac{1}{r} \right\rangle = \frac{2Z}{a_0}$$

The Hamiltonian of the system is given by

$$\hat{H} = \frac{1}{2m}(p_1^2 + p_2^2) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

Therefore

$$E(Z) = \langle \hat{H} \rangle = \frac{1}{2m}\langle p_1^2 + p_2^2 \rangle - \frac{2e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle + \frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r_{12}} \right\rangle = -2R\left(4Z - Z^2 - 5Z/8\right)$$

By completion of square:

$$E(Z) = 2R\left(Z - \frac{27}{16}\right)^2 - 2R\cdot\left(\frac{27}{16}\right)^2 \geqslant -2R\cdot\left(\frac{27}{16}\right)^2 \approx -77.84 \text{ eV}$$

We deduce that the ground state energy is lower than -77.84 eV. Then the first ionization energy is higher than $77.74 - 54.4 = 23.34$ eV. ☐

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Question 4

Two of the energy levels in Helium have the standard notation $1s^1 2s^1\ {}^1S_0$ and $1s^1 2s^1\ {}^3S_1$. Explain every part of this notation. The difference in the notation for the two levels stresses a difference in the spin part of the wavefunction, but the spatial part is also different: what is the important distinguishing feature between the two spatial wavefunctions?

Solution. By solving time-independent Schrödinger's equation for hydrogen-like atoms, we can label the eigenstates of the electrons by $|n, \ell, m, s\rangle$. The orbitals with distinct energies and orbital angular momenta are represented by $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$... The number on the left is n and the letter on the right ~~indicates~~ ℓ (s for $\ell = 0$, p for $\ell = 1$, d for $\ell = 2$ and f for $\ell = 3$). We put a number on the right upper index to indicate the number of electrons occupying the orbital. So $1s^1 2s^1$[illegible]plies that one electron is occupying $1s$ orbital and the other is occupying $2s$ orbital.

Next we use a captial letter to indicate the total orbital angular momentum of the electrons (S for $L = 0$, P for $L = 1$, etc.). We put a ~~number~~ $2S + 1$ on the left upper index and a number $J = L + S$ on the right lower index, where S is the total spin and J is the total angular momentum. So ${}^1S_0$ means that $L = 0$, $S = 0$ and $J = 0$, and ${}^3S_1$ means that $L = 0$, $S = 1$, and $J = 1$.

For the state $1s^1 2s^1\ {}^1S_0$, the spins of the two electrons are in the opposite direction, whereas the spins are aligned for the state $1s^1 2s^1\ {}^3S_1$. A qualitative argument is that, if the spins are aligned, then by Pauli exclusion principle the electrons tend to avoid each other in space, leading to a lower ~~potential due~~ to electron-electron repulsion. ☐

Question 5

Recall Qu. 7.6 from Prof Blundell's problem sets, which reads as follows.

> *A is a beam of atoms with spin-1/2 with the spin alined along the $+x$-axis. B is a beam of similar unpolarised atoms. A and B are separately passed through a Stern-Gerlach apparatus aligned along z. In each case you get two emerging beams coming out of the Stern-Gerlach experiment. Is there any difference between the two cases? If so, how could you detect that experimentally?*

Write down density matrices in the z-basis to describe the beams A and B before passage through the Stern-Gerlach apparatus. Use these density matrices to evaluate $\langle \hat{s}_x \rangle$ and $\langle \hat{s}_z \rangle$ for each beam.

Solution. In the z-basis, we have:

$$|{\rightarrow}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \qquad |{\leftarrow}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

The density matrix of A:

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$$\hat{\rho}_A = |{\rightarrow}\rangle\langle{\rightarrow}| = \frac{1}{2}\begin{pmatrix}1\\1\end{pmatrix}\begin{pmatrix}1 & 1\end{pmatrix} = \frac{1}{2}\begin{pmatrix}1 & 1\\1 & 1\end{pmatrix}$$

The density matrix of B:

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$$\hat{\rho}_B = \frac{1}{2}(|{\rightarrow}\rangle\langle{\rightarrow}| + |{\leftarrow}\rangle\langle{\leftarrow}|) = \frac{1}{4}\begin{pmatrix}1\\1\end{pmatrix}\begin{pmatrix}1 & 1\end{pmatrix} + \frac{1}{4}\begin{pmatrix}1\\-1\end{pmatrix}\begin{pmatrix}1 & -1\end{pmatrix} = \frac{1}{2}\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} = \frac{1}{2}\hat{\mathrm{id}}$$

In the z-basis, $\hat{s}_x$ and $\hat{s}_z$ are represented by the Pauli matrices:

$$\sigma_x = \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} \qquad \sigma_z = \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$

Hence for A:

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$$\langle \hat{s}_x \rangle_A = \mathrm{tr}(\hat{\rho}_A \hat{s}_x) = \frac{1}{2}\,\mathrm{tr}\left(\begin{pmatrix}1 & 1\\1 & 1\end{pmatrix}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\right) = 1, \qquad \langle \hat{s}_z \rangle_A = \mathrm{tr}(\hat{\rho}_A \hat{s}_z) = \frac{1}{2}\,\mathrm{tr}\left(\begin{pmatrix}1 & 1\\1 & 1\end{pmatrix}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\right) = 0.$$

For B:

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$$\langle \hat{s}_x \rangle_B = \mathrm{tr}(\hat{\rho}_B \hat{s}_x) = \frac{1}{2}\,\mathrm{tr}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} = 0, \qquad \langle \hat{s}_z \rangle_B = \mathrm{tr}(\hat{\rho}_B \hat{s}_z) = \frac{1}{2}\,\mathrm{tr}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} = 0.$$

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