

Advanced Quantum Mechanics SS 2024

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Sheet 01: Identical Particles (to be handed in by 08.05.2024)

1 Gaussian packets of identical particles

In this exercise we will consider a system of two identical particles in one dimension. Suppose the spatial wave function of the two particles is made out of two gaussians peaked around $x_{\pm} = \pm a$,

$$\psi_{\pm} = N \exp\left(-\frac{\mu^2}{2}(x \pm a)^2\right). \quad (1)$$

Consider the case of two fermions of spin-1/2 and assume that the spins of the two particles are aligned, $S_z^{(1)} = S_z^{(2)}$.

1. Build a properly normalised wave function for this system.
2. Compute the probability density, $\rho(x)$, for the separation between the two particles $x = x_1 - x_2$.
3. Compute the expectations $\langle x \rangle$ and $\langle x^2 \rangle$. Discuss the limits $\mu \gg 1$ and $a \ll 1$.

Consider now the case of two spin-0 bosons and repeat the exercise.

1. Discuss the behaviour of $\rho(x)$ in the fermionic and bosonic case: how do the positions of extrema change varying the parameters μ and a ?

2 Helium atom and energy splitting

Consider a Helium atom. In the lecture, we first neglected electron-electron interaction and treated Helium as a double-copy of Hydrogen, with different atomic number. We then included its effect in perturbation theory and derived the energy shift for the the ground state, which has two electron with quantum numbers $n = 1, l = 0, m = 0$. The spatial wave-function cannot be antisymmetric, therefore the spin state must be a singlet.

Here we consider the first excited state, in which one electron has quantum number $n = 1, l = 0, m = 0$ and the other $n = 2, l = (0, 1), m = (0, -1, 1)$. In this case, both spin-triplet and -singlet state are admitted, and the spatial wave function is (anti-)symmetric, accordingly. Neglecting electron-electron interactions, all these states are degenerate in energy. We used perturbation theory to compute the energy-shift due to the the electron-electron interaction. For the first excited state, we found

$$\Delta E_1^s = J_l + K_l, \quad (2)$$

for the spin-singlet states, and

$$\Delta E_1^t = J_l - K_l, \quad (3)$$

for the spin-triplet states, where

$$J_l = \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}_1 \int d\vec{r}_2 \frac{|\phi_{100}(\vec{r}_1)|^2 |\phi_{2l0}(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}, \quad (4)$$

and

$$K_l = \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\phi_{100}^*(\vec{r}_1)\phi_{100}(\vec{r}_2)\phi_{2l0}^*(\vec{r}_1)\phi_{2l0}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}. \quad (5)$$

1. Give a general formula for these two classes of integrals keeping l generic (do not perform the radial integration).
2. Consider the cases $l = 0, 1$ and perform the final integration.
3. Discuss the result.

3 Hund's Rules

Hund's rules are a set of three empirical rules that allow to determine the electronic configuration of the ground state of multi-electron atoms. The notation used to identify the state is $^{2S+1}L_J$, where S , L are respectively the total spin and orbital angular momenta, and $J = L + S$. According to the spectroscopic notation the possible values of the L quantum number are identified by the letters $L = S, P, D, F, G, \dots$ for $L = 0, 1, 2, 3, 4, \dots$. Hund's rules can be summarised as

1. The state with largest S lies lowest in energy.
2. For a given S , the state with the highest L lies lowest.
3. For a given L and S , if the incomplete shell is not more than half-filled, the lowest state has the minimum value of $J = |L - S|$; if the shell is more than half-filled, the state of lowest energy has $J = |L + S|$.

Use Hund's rules to find the ground states of Nitrogen (N), Aluminium (Al) and Titanium (Ti) starting from the electronic configuration that you can find on any periodic table.

4 Appendix: special functions

The eigenfunction for a central potential can be written as

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m}(\theta, \phi), \quad (6)$$

where the function $Y_{l,m}(\theta, \phi)$ are the spherical harmonics, defined in terms of the associated Legendre polynomials, P_l^m , as

$$Y_{l,m}(\theta, \phi) = C_{l,m} e^{im\phi} P_l^{(m)}(\cos \theta), \quad (7)$$

where $C_{l,m}$ and P_l^m are real. For $m = 0$,

$$Y_{l,0}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l^{(0)}(\cos \theta), \quad (8)$$

$$P_l^{(0)}(u) = (-1)^l \frac{1}{2^l l!} \left(\frac{d}{du}\right)^l (1-u^2)^l \quad (9)$$

They satisfies

$$\text{Orthogonality 1:} \quad \int_0^{2\pi} d\phi \int_{-1}^1 d \cos(\theta) Y_{l,m}^*(\theta, \phi) Y_{k,n}(\theta, \phi) = \delta_{lk} \delta_{mn}, \quad (10)$$

$$\text{Orthogonality 2:} \quad \int_{-1}^1 du P_l^{(0)}(u) P_k^{(0)}(u) = \delta_{lk} \frac{2}{2l+1}, \quad (11)$$

$$\text{Addition:} \quad P_l^0(\vec{r} \cdot \vec{r}') = \frac{4\pi}{2l+1} \sum_{m=-l}^m Y_{l,m}(\theta, \phi) Y_{l,m}(\theta', \phi'). \quad (12)$$

where in the addition formula (θ, ϕ) and (θ', ϕ') are the spherical coordinates for \vec{r} and \vec{r}' . In the case of the Hydrogen-like atom, the first radial functions are:

$$\begin{aligned} R_{10}(r) &= 2\left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0), \\ R_{20}(r) &= 2\left(\frac{Z}{2a_0}\right)^{3/2} \left(1 - \frac{Zr}{2a_0}\right) \exp(-Zr/2a_0), \\ R_{21}(r) &= \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0} \exp(-Zr/2a_0). \end{aligned} \quad (13)$$

Finally, the following expansion will be useful

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_1} \sum_{L \geq 0} \left(\frac{r_2}{r_1}\right)^L P_L^{(0)}(\cos \theta) \quad \text{for } r_1 > r_2. \quad (14)$$