Kvantmehaanika ja spektroskoopia

Küsimused loeng 10-13

8. Can you prove expression $\left[\widehat{H}, \widehat{L^2}\right] = 0$. What does it mean from a physical point of view? How is this equation related to Heisenberg's uncertainty principle? Here $\widehat{H} = -\frac{\hbar^2}{2m}\Delta$.

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To prove the expression, we must see whether the operators commute.

When we look at the Laplace operator, it is clear that the first part of the operator only acts on the r vector, and as the squared angular momentum operator acts on the angles, they are independent of each other and therefore commute. The second part of the Laplace operator contains the squared angular momentum operator in it, but an operator applied to itself always commutes. It also contains $\frac{1}{r^2}$ which again only applies to the r vector and therefore is

independent from the angles that the squared angular momentum operator acts upon. All together the second part of the Laplacian also commutes, which proves that the whole expression is true.

The Laplace operator is as follows: $\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left(-\frac{1}{\hbar^2} \widehat{L^2} \right)$ and the squared angular momentum operator is $\widehat{L^2} = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]$

In a physical point of view it means that in spherically symmetric situations, the Hamiltonian is invariant to rotations. That also means that angular momentum is conserved when the observed particle is in a central potential.

As they commute, it means that the Heisenberg's uncertainty does not apply here and the eigenvalues of total energy and total orbital angular momentum squared can be known simultaneously. Although, it must be noted that we can only know one of the components of L along with the L squared, here the uncertainty applies again. Through L squared we also get orbital quantum number *l*.

14. How can the angle between the angular momentum vector \overline{L} and the z-axis becalculated in quantum mechanics? Calculate the allowed possible values of this anglefor 2p orbital.20

The L vector is usually represented as a vector that precesses around the z axis. It makes up the shell of a cone, and the angle between it and the z axis is calculated as follows:

The length of the L vector is $|\overline{L}| = \hbar \sqrt{l(l+1)}$ where l = 0, 1, ... and the projection to z axis is $L_z = \hbar m$ where $m = 0, \pm 1, \pm 2, ...$ That would mean that the angle θ can be calculated

thusly: $\theta = \arccos\left(\frac{L_z}{|\overline{L}|}\right) = \arccos\left(\frac{m}{\sqrt{l(l+1)}}\right)$.

In 2p orbital the values are l = 1 and m = -1, 0, +1. Then the angles become $\theta_1 = \arccos\left(\frac{-1}{\sqrt{1(1+1)}}\right) = 135^\circ, \ \theta_2 = \arccos\left(\frac{0}{\sqrt{1(1+1)}}\right) = 90^\circ \text{ and } \ \theta_3 = \arccos\left(\frac{1}{\sqrt{1(1+1)}}\right) = 45^\circ$

26. How to calculate ionization energy of an electron of the states 3s and 4p?

To calculate ionization energies for 3s we will take the quantum number n to be 3 and in state 4p it will be 4.

The equation for energy states is $E_n = -\frac{Mb^2e^4}{2\hbar^2} \frac{1}{n^2}$ where n = 1, 2,... is the quantum number, $b = \frac{1}{4\pi\epsilon_0}$. The equation can also be simplified a bit by using Rydberg constant $R = \frac{Mb^2e^4}{2\hbar^3} \approx 2,07 \cdot 10^{16} \text{s}^{-1}$, so the final equation looks like so: $E_n = -R\hbar \frac{1}{n^2}$. 20 Now, knowing this, ionization energy for state 3s is: $E_3 = -2,07 \cdot 10^{16} \cdot 1,05 \cdot 10^{-34} \frac{1}{3^2} = -2.415 \cdot 10^{-19} [J] \approx 1.507 eV$

And for state 4p it is:

 $E_4 = -2,07 \cdot 10^{16} \cdot 1,05 \cdot 10^{-34} \frac{1}{4^2} = -1.358 \cdot 10^{-19} [J] \approx 0.848 eV$

34. What does the electron configuration for N, CI and K atoms look like? Why?

Nitrogen (N) has the electron configuration: $1s^22s^22p^3$. Nitrogen has 7 protons, therefore it needs 7 electrons to be neutral. It has three electrons less than needed to fill the 2p orbital.

Chlorine (CI) has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^5$. Chlorine has 17 protons, so it needs 17 electrons to be neutral. It has 5 electrons in 3p orbital, which means that it has affinity to gaining one more electron.

Potassium (K) has the electron configuration: $1s^22s^22p^63s^23p^64s^1$. Potassium has 19 protons, so it also has 19 electrons to be neutral. As the 4s orbital only has one electron, it gives it away to form bonds with other atoms.

The way the electrons are in different atoms is based on two principles: Pauli exclusion principle which states that each quantum state may only be occupied by two electrons; and the principle that the ground state is minimal, which means that electrons start filling orbitals from the lowest possible energy state.

41. Write Schrödinger's equation for zero order approximation of perturbation theory.

The zero(th) order approximation for perturbation theory is approximation without perturbation - unperturbed system. So if we take the eigenvalue problem for $\widehat{H_0}$:

 $\widehat{H_0}\Psi_n = E_n\Psi_n$ and assume that it is solved so that we have possible energy values E_1 , E_2 , ... and corresponding eigenfunctions Ψ_1 , Ψ_2 , ...

In that case the time dependent Schrödinger equation's $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi$ general solution can be presented as a linear combination $\Psi(\bar{r}, t) = \sum c_n e^{-\frac{i}{\hbar}E_n t} \Psi_n(\bar{r})$ where c_1 , c_2 , ... are some constants.