Approximate Methods in Quantum Chemistry
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Lecture- 24
Excited States of He Atom-II

Hello students! Welcome to this lecture. In the last lecture, we discussed the treatment of excited states of helium atom with degenerate perturbation theory. We will continue our discussion from there.

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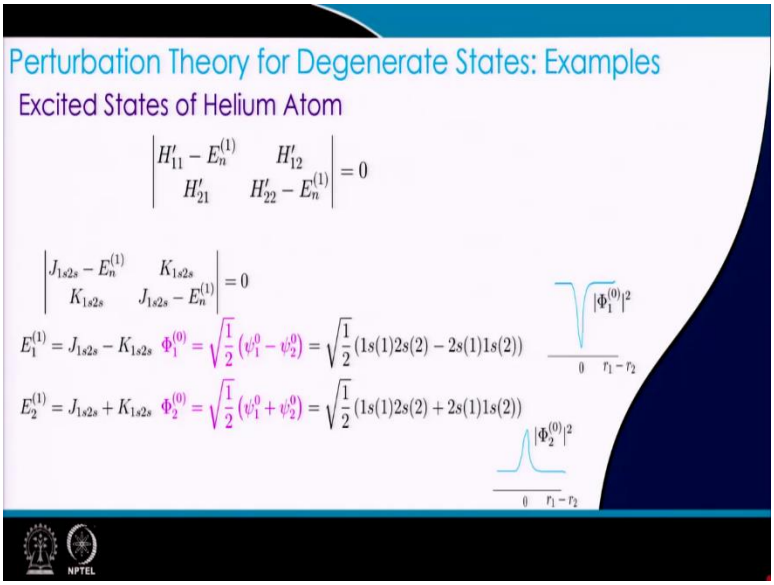

Just to refresh your memory, for the 1st excited state of helium atom, we formulated a 8x8 problem, since we found that in the absence of electron-electron interaction, the 1st excited state of He is 8-fold degenerate. After formulating the 8x8 secular determinant and evaluating the matrix elements, we found that this 8x8 problem can be divided to 4 independent 2x2 problems. Of the four problems, we considered one 2x2 problem and obtained the energy (1st order energy correction) and wave functions.

So, the problem at hand became somewhat a simpler problem, a 2 by 2 problem, where the matrix elements H'_{11} or H'_{12} were evaluated as Coulomb integral (J_{1s2s}) or the exchange integral (K_{1s2s}).

The energy corrections show lifting of degeneracy between the two levels. While discussing the wave functions, we came across the Fermi hole (found in $\Phi_1^{(0)}$) and Fermi heap (found in $\Phi_2^{(0)}$). While the Fermi hole describes the situation where the two electrons of He atom are not expected to be found at the same spatial position, the Fermi heap describes the opposite situation, i.e., an increased probability of the electron 2 to be found where electron 1 is present. Both Fermi hole and Fermi heap have pure quantum mechanical origin and we can rationalize the two in the following discussion.

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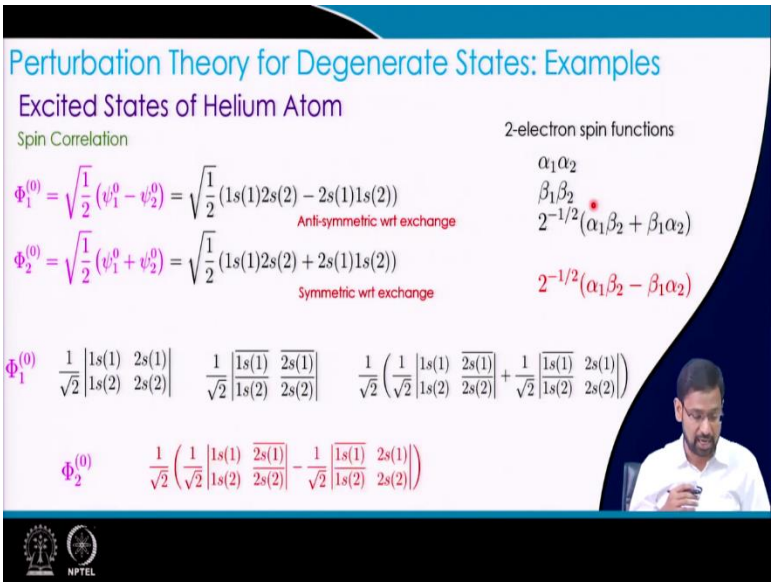

For a many-electron system, a well-behaved function must be antisymmetric with respect to electron exchange. To verify this, we need to include the spin part of the problem, which has so far been neglected. For a 2-electron system, the complete set of spin functions are given by a symmetric (with-respect to electron exchange) triplet pair

$$\alpha_1\alpha_2$$
$$\beta_1\beta_2$$
$$2^{-1/2}(\alpha_1\beta_2+\beta_1\alpha_2)$$

and an antisymmetric singlet function $2^{-1/2}(\alpha_1\beta_2-\beta_1\alpha_2)$

The spatial functions $\Phi_1^{(0)}$ *and* $\Phi_2^{(0)}$ are anti-symmetric and symmetric, respectively, with-respect to electron exchange. To form overall anti-symmetric wave functions, we need to

couple the (spatially) symmetric functions with (spin) anti-symmetric functions and vice versa.

Therefore, $\Phi_1^{(0)}$ forms a triplet pair given by the following three determinantal wave functions:

$$\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & 2s(1) \\ 1s(2) & 2s(2) \end{vmatrix} \qquad \frac{1}{\sqrt{2}}\begin{vmatrix} \overline{1s(1)} & \overline{2s(1)} \\ \overline{1s(2)} & \overline{2s(2)} \end{vmatrix} \qquad \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & \overline{2s(1)} \\ 1s(2) & \overline{2s(2)} \end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix} \overline{1s(1)} & 2s(1) \\ \overline{1s(2)} & 2s(2) \end{vmatrix}\right)$$

The first wave function considers both the electrons in α spin and the second wave function shows both electrons in β spin (denoted by an overbar on the 1s or 2s orbital). The third function is obtained by considering $\alpha_1\beta_2 + \beta_1\alpha_2$ spin function. This determinant way of writing the anti-symmetric wave functions is called Slater determinant, where the orbitals 1s or $\overline{1s}$ are called spinorbitals (as opposed to (spatial) orbitals). On the other hand, $\Phi_2^{(0)}$ forms a singlet pair given by the following Slater determinant,

$$\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & \overline{2s(1)} \\ 1s(2) & \overline{2s(2)} \end{vmatrix} - \frac{1}{\sqrt{2}}\begin{vmatrix} \overline{1s(1)} & 2s(1) \\ \overline{1s(2)} & 2s(2) \end{vmatrix}\right)$$

The above wave function is antisymmetric with respect to electron exchange and represents a singlet spin multiplicity where the two electrons have opposite spin. This now explains the observed Fermi heap in $\Phi_2^{(0)}$, where two electrons occupy the same spatial (orbital) location, while having opposite spin.

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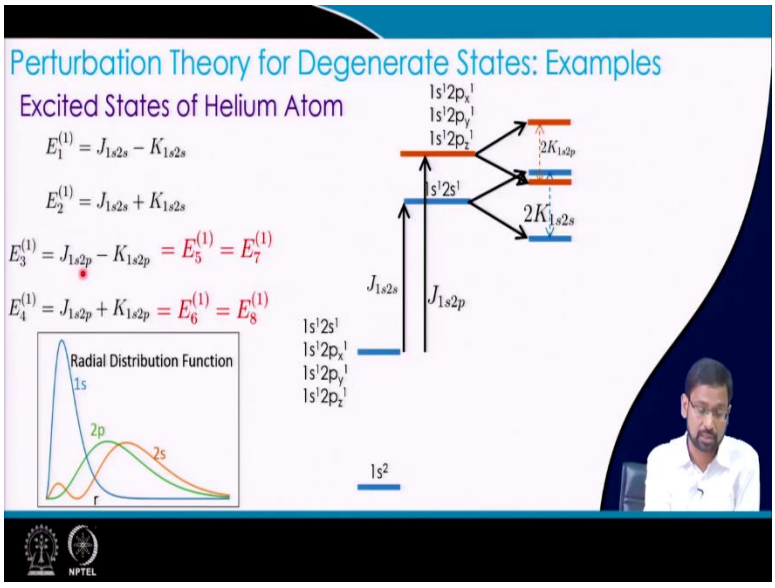

Next, let us discuss the excited state energy levels of He atom. In the absence of electron-electron repulsion, the 1st excited state is 8-fold degenerate. The 1st order energy corrections for the E_1 and E_2 levels are obtained by solving the first of the four 2x2 problems:

$$E_1^{(1)} = J_{1s2s} - K_{1s2s}$$

$$E_2^{(1)} = J_{1s2s} + K_{1s2s}$$

Similarly, if we solve the second 2x2 problem, we will obtain similar results, such as:

$$E_3^{(1)} = J_{1s2p} - K_{1s2p}$$

$$E_4^{(1)} = J_{1s2p} + K_{1s2p}$$

Here the Coulomb integrals and exchange integrals are obtained when the two electrons are considered in 1s and $2p_x$ orbitals. Since the Coulomb and exchange integrals are going to be same if one of the electrons is in $2p_x$ or $2p_y$ or $2p_z$ orbital, we have dropped x from the $2p_x$ notation in the above equation. It is therefore obvious that $E_3^{(1)} = E_5^{(1)} = E_7^{(1)}$ and $E_4^{(1)} = E_6^{(1)} = E_8^{(1)}$.

Comparing the above expressions of the 1st order energy correction, it is seen that all energy levels are raised by the Coulomb interaction (E_1 and E_2 are raised by J_{1s2s} and E_3 to E_8 are raised by J_{1s2p}). If we ignore the exchange integral, we can see that the 8-fold degeneracy is lifted to two different levels, one with 2-fold degeneracy and the other with 6-fold degeneracy.

By comparing the radial distribution functions of 1s, 2s and 2p orbitals of hydrogen atom (shown in the the slide above), you would see that the electron in the 2s orbital has got higher probability to be found closer to the nucleus compared to 2p. In other words, 2s electron can penetrate closer to the nucleus as compared to 2p electron. This means that 1s electron shields the 2s electron from the nucleus less effectively than 2p electron. The Coulomb interaction arises when the electrons repel each other. Now when it comes to 2s electron, it will face the repulsion from that part of the 1s charge cloud which is yet not penetrated. Since the 2s electron is able to penetrate over the 1s charge density, this Coulomb interaction is less. On the other hand, 2p electron cannot penetrate so close to the

nucleus and therefore, the Coulomb interaction or the charge repulsion between 1s and 2p is going to be greater than what we see between 1s and 2s. Therefore, $J_{1s2p} > J_{1s2s}$.

Now let us introduce the exchange interaction. First, we will look at the K_{1s2s} interaction. When we add this exchange interaction, we would see that the states (E_1 and E_2) will split by $2K_{1s2s}$. The two-fold degeneracy is now lifted to the lower energy triplet state (^{3}S in spectroscopic notation) and upper energy singlet state (^{1}S). Similarly, the 6-fold degenerate energy levels (E_3 to E_8) would split to two groups (^{3}P and ^{1}P) separated by $2K_{1s2p.}$ Each of these two groups is 3-fold degenerate, since the exchange integral between 1s and $2p_x$ is same that between 1s and $2p_y$ as well as 1s and $2p_z$. This degeneracy due to the magnetic quantum numbers can be lifted only when we apply an external filed, but not with internal electron-electron interaction.

The ^{1}S and ^{3}P have very similar energy. Within 1st order perturbation correction, we ^{3}P lower in energy than ^{1}S. However, with higher order energy correction, this ordering changes.

Thank you for your attention.