Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture- 23
Excited States of He Atom-I

Hello students! Welcome to this lecture. In the last lecture, we discussed how to treat degenerate states with perturbation theory. We also discussed its application to the excited states of He atom. In this lecture, we will continue our discussion on the excited states of He atom.

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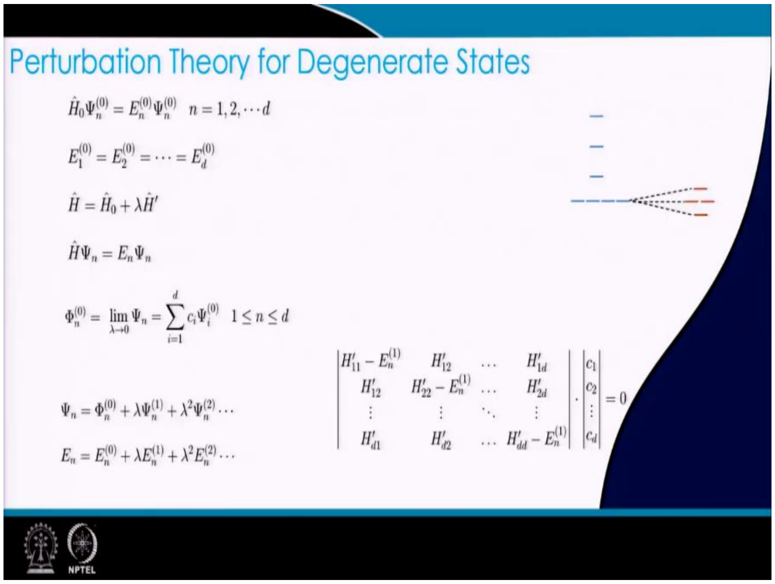

Perturbation Theory for Degenerate States

$$\hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \quad n = 1, 2, \cdots d$$

$$E_1^{(0)} = E_2^{(0)} = \cdots = E_d^{(0)}$$

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

$$\hat{H}\Psi_n = E_n\Psi_n$$

$$\Phi_n^{(0)} = \lim_{\lambda\to 0}\Psi_n = \sum_{i=1}^{d} c_i\Psi_i^{(0)} \quad 1 \le n \le d$$

$$\Psi_n = \Phi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)}\cdots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\cdots$$

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \cdots & H'_{1d} \\ H'_{12} & H'_{22} - E_n^{(1)} & \cdots & H'_{2d} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{d1} & H'_{d2} & \cdots & H'_{dd} - E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_d \end{vmatrix} = 0$$

Although we made some progress along this direction in our last lecture, to keep continuity of discussion, we will quickly go through some of the important points discussed in the last lecture. We learnt in the earlier class that when we have a system with several degenerate states, the standard perturbation theory cannot be applied. For a *d*-fold degenerate system, when we consider perturbation, the degeneracy may be lifted partially or completely. However, in the limit of vanishing perturbation, we cannot trace back to one of these degenerate states, since any linear combination of these degenerate eigenfunctions is also an eigenfunction with the same eigenvalue. To avoid this problem, we defined the unperturbed wave functions as a linear combination of the degenerate eigenfunctions. The coefficients of the linear combination are to be determined.

Using the above defined unperturbed wave function, we formulated the perturbation theory within which the wave function correction and energy correction were obtained. While looking at 1st order energy correction, we came across a *d* x *d* secular determinant (see above in the slide) whose solution gives the 1st order energy correction as well as the coefficients to be used for the linear combination in expressing the unperturbed wave function.

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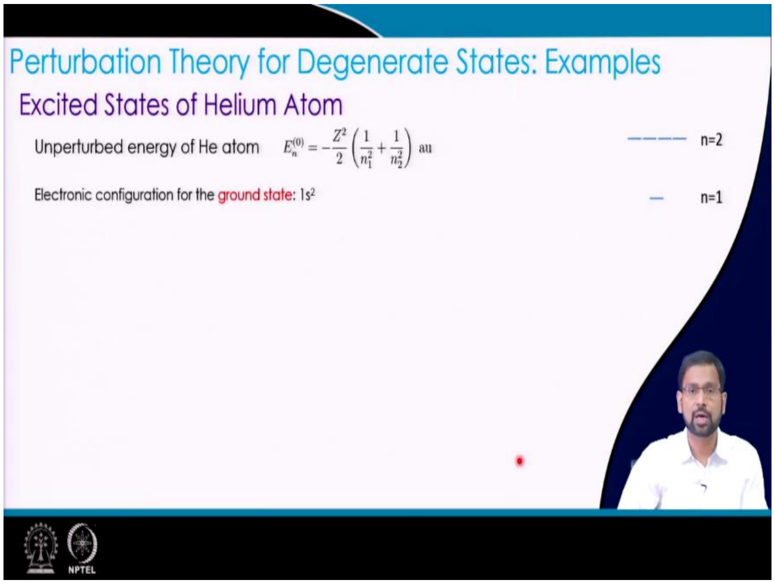

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Unperturbed energy of He atom $E_n^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$ au

Electronic configuration for the ground state: $1s^2$

We used the above strategy to study the excited states of He atom. Here, we considered electron-electron interaction as the perturbation. In the absence of the perturbation, the Hamiltonian is sum of two 1-electronic (He^+) systems, whose exact solution is possible. For this system, the energy of the system is given by ($Z = 2$),

$$E_n^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right) \text{ au}$$

The ground state is obtained when $n_1 = n_2 = 1$, i.e., the electron configuration is $1s^2$.

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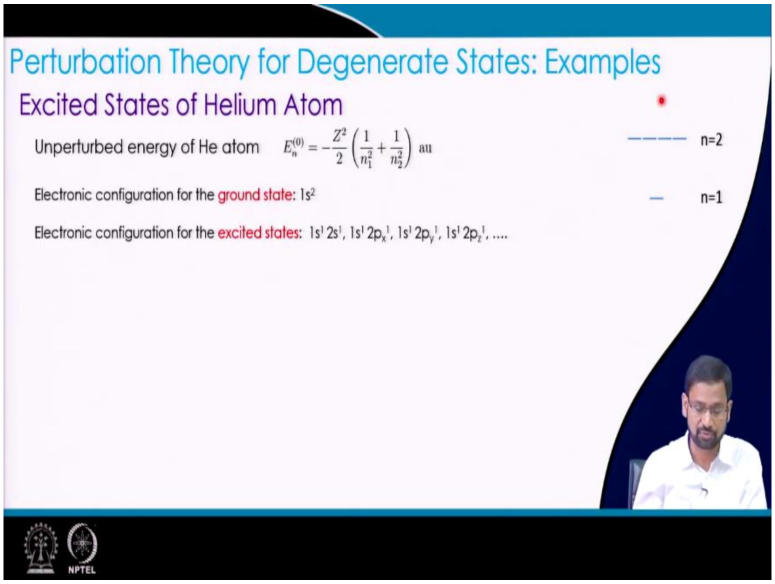

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Unperturbed energy of He atom $E_n^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$ au

Electronic configuration for the ground state: $1s^2$

Electronic configuration for the excited states: $1s^1\,2s^1$, $1s^1\,2p_x^1$, $1s^1\,2p_y^1$, $1s^1\,2p_z^1$, ...

Since we are interested in the excited states of He atom, we can construct wave functions for the excited state by promoting one electron from $n = 1$ to $n = 2$. Since $n = 2$ is 4-fold degenerate (2s, $2p_x$, $2p_y$, and $2p_z$), we can generate 4-degenerate configurations $1s^1\,2s^1$, $1s^1\,2p_x^1$, $1s^1\,2p_y^1$, $1s^1\,2p_z^1$. For higher excited states, we can promote one electron to $n = 3$, 4, etc. We restrict our discussion here only to the first excited state.

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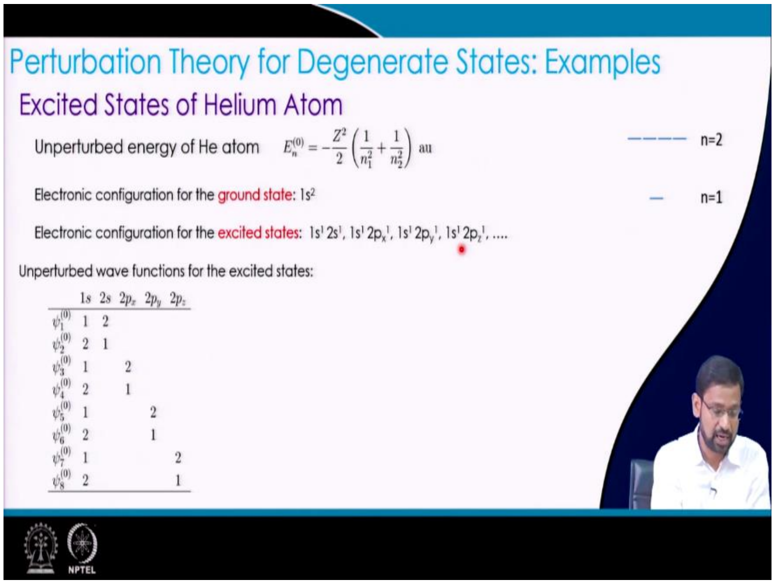

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Unperturbed energy of He atom $E_n^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$ au

Electronic configuration for the ground state: $1s^2$

Electronic configuration for the excited states: $1s^1\,2s^1$, $1s^1\,2p_x^1$, $1s^1\,2p_y^1$, $1s^1\,2p_z^1$, ...

Unperturbed wave functions for the excited states:

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

To incorporate electron indistinguishability, we can generate four more electron configurations by exchanging the electrons between n =1 and n=2 in the original set of 4-wave functions. This gives rise to eight degenerate wave functions as shown above in the slide.

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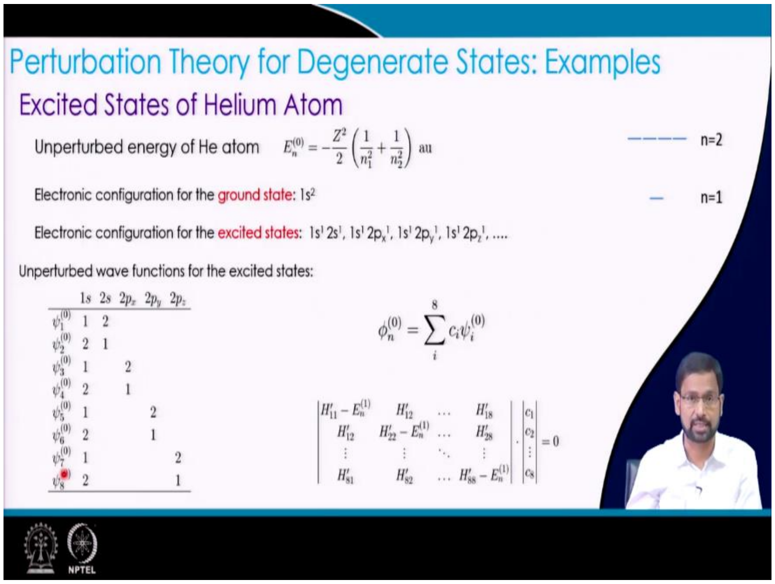

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Unperturbed energy of He atom $E_n^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$ au

Electronic configuration for the ground state: $1s^2$

Electronic configuration for the excited states: $1s^1 2s^1$, $1s^1 2p_x^1$, $1s^1 2p_y^1$, $1s^1 2p_z^1$, ...

Unperturbed wave functions for the excited states:

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

$$\phi_n^{(0)} = \sum_i^8 c_i \psi_i^{(0)}$$

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} & \cdots & H'_{18} \\ H'_{12} & H'_{22}-E_n^{(1)} & \cdots & H'_{28} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{81} & H'_{82} & \cdots & H'_{88}-E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_8 \end{vmatrix} = 0$$

We are now dealing with 8-fold degenerate system in the excited state of He atom without including the electron-electron interaction. We can define our unperturbed system as a linear combination of these eight degenerate wave functions.

$$\phi_n^{(0)} = \sum_i^8 c_i \psi_i^{(0)}$$

The above form of the wave function leads to a 8x8 secular determinant

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} & \cdots & H'_{18} \\ H'_{12} & H'_{22}-E_n^{(1)} & \cdots & H'_{28} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{81} & H'_{82} & \cdots & H'_{88}-E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_8 \end{vmatrix} = 0$$

whose solution would give the 1st order correction to energy ($E_n^{(1)}$) and the coefficients (c_i). In order to solve this problem, we need to evaluate the energy integrals ($H_{ij}^{'}$). Since the basis functions (the wave functions of He$^+$) are orthonormal, we do not have to evaluate the overlap integrals in the present case.

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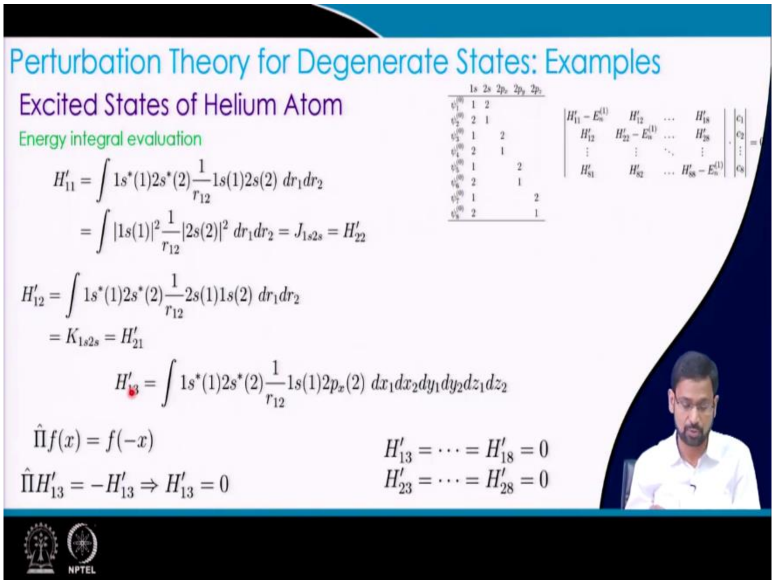

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Energy integral evaluation

	1s	2s	$2p_x$	$2p_y$	$2p_z$
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} & \cdots & H'_{18} \\ H'_{12} & H'_{22}-E_n^{(1)} & \cdots & H'_{28} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{81} & H'_{82} & \cdots & H'_{88}-E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_8 \end{vmatrix} =$$

$$H'_{11} = \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}1s(1)2s(2)\ dr_1dr_2$$
$$= \int |1s(1)|^2\frac{1}{r_{12}}|2s(2)|^2\ dr_1dr_2 = J_{1s2s} = H'_{22}$$

$$H'_{12} = \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}2s(1)1s(2)\ dr_1dr_2$$
$$= K_{1s2s} = H'_{21}$$

$$H'_{13} = \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}1s(1)2p_x(2)\ dx_1dx_2dy_1dy_2dz_1dz_2$$

$$\hat{\Pi}f(x) = f(-x)$$

$$\hat{\Pi}H'_{13} = -H'_{13} \Rightarrow H'_{13} = 0$$

$$H'_{13} = \cdots = H'_{18} = 0$$
$$H'_{23} = \cdots = H'_{28} = 0$$

The solution of the above mentioned 8x8 secular determinant requires evaluation of several energy integrals, $H'_{ij} = \langle\psi_i^{(0)}|\ \hat{H}'\ |\psi_j^{(0)}\rangle$.

First let us evaluate, $H'_{11} = \langle\psi_1^{(0)}|\ \hat{H}'\ |\psi_1^{(0)}\rangle$

$$H'_{11} = \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}1s(1)2s(2)\ dr_1dr_2$$
$$= \int |1s(1)|^2\frac{1}{r_{12}}|2s(2)|^2\ dr_1dr_2 = J_{1s2s} = H'_{22}$$

The above integral is a Coulomb integral (J) representing a Coulomb interaction between the electron density of electron 1 in 1s orbital and electron density of electron 2 in 2s orbital.

Next, let us consider

$$H'_{12} = \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}2s(1)1s(2)\ dr_1dr_2$$
$$= K_{1s2s} = H'_{21}$$

Unlike H'_{11}, the above integral cannot be expressed as a classical Coulomb integral, since the electrons (electron 1 or 2) are exchanged between the orbitals. Such a term appears because we have considered electron exchange in our starting wave function. Therefore, the resulting integral is called as the exchange integral (*K*).

Now, let us consider

$$H'_{13} = \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}1s(1)2p_x(2)\ dx_1dx_2dy_1dy_2dz_1dz_2$$

In the above integral, instead of writing dr_1 dr_2, we have actually expanded it in terms of dx_1 dy_1 dz_1 for electron 1 and similarly dx_2 dy_2 dz_2 for electron 2. Before trying to evaluate the numerical value of the integral, let us evaluate its symmetry properties, with respect to the parity operator (whose eigenfunctions are all even and all odd functions with eigenvalues of 1 and -1, respectively). For the above integral to be non-zero it has to be totally symmetric. However, we can see that in the above integral, $2p_x(2)$ function is anti-symmetric with respect to x_2 coordinate, while all other terms are symmetric. Hence, the overall integral becomes anti-symmetric and thus vanishes. Similarly, we can show that not only H'_{13}, but also $H'_{14} = H'_{15} = H'_{16} = H'_{17} = H'_{18} = 0$. Similarly, $H'_{23} = \ldots = H'_{28} = 0$.

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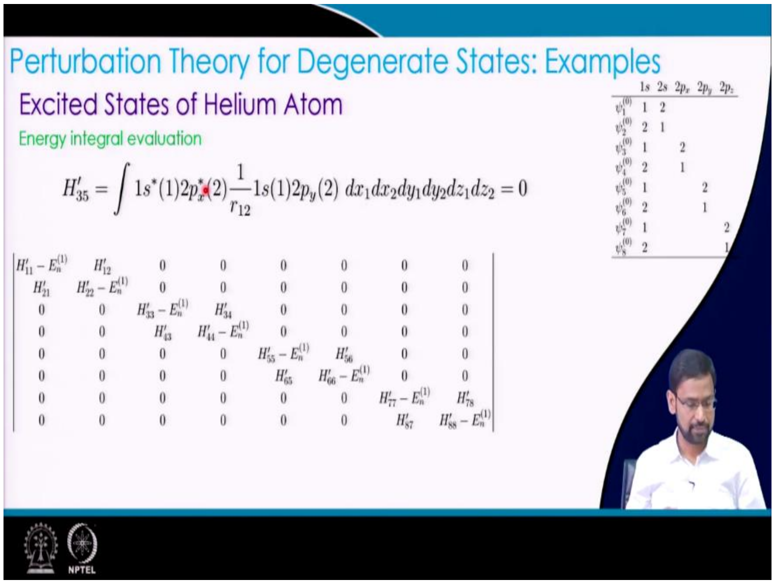

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Energy integral evaluation

$$H'_{35} = \int 1s^*(1)2p_x^*(2)\frac{1}{r_{12}}1s(1)2p_y(2)\ dx_1dx_2dy_1dy_2dz_1dz_2 = 0$$

	1s	2s	$2p_x$	$2p_y$	$2p_z$
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\ H'_{21} & H'_{22}-E_n^{(1)} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & H'_{33}-E_n^{(1)} & H'_{34} & 0 & 0 & 0 & 0 \\ 0 & 0 & H'_{43} & H'_{44}-E_n^{(1)} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H'_{55}-E_n^{(1)} & H'_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & H'_{65} & H'_{66}-E_n^{(1)} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & H'_{77}-E_n^{(1)} & H'_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & H'_{87} & H'_{88}-E_n^{(1)} \end{vmatrix}$$

Following the discussion of $H'_{11} = H'_{22} = J_{1s2s}$, we can show that other diagonal matrix elements will have similar form, for example, $H'_{33} = H'_{44} = J_{1s2px}$, $H'_{55} = H'_{66} = J_{1s2py}$, and so on. Similarly, we can also show that the determination of the matrix elements H'_{34}, H'_{56}, and H'_{78} are going to be similar to that of H'_{12} (= K_{1s2s}). These integrals correspond to the basis functions which are simply different from each other in electron exchange. We can express these elements as the exchange integrals, e.g., $H'_{34} = K_{1s2px}$, $H'_{56} = K_{1s2py}$, and $H'_{78} = K_{1s2pz}$.

Next, let us consider H'_{35} as the following integral involving ψ_3 and ψ_5

$$H'_{35} = \int 1s^*(1)2p_x^*(2)\frac{1}{r_{12}}1s(1)2p_y(2)\ dx_1dx_2dy_1dy_2dz_1dz_2 = 0$$

We can use similar symmetry arguments (discussed earlier) to show that this matrix element is 0 (due to presence of $2p_x(2)$ and $2p_y(2)$ functions in the integral). Similarly, we can also show $H'_{36} = H'_{37} = H'_{38} = 0$.

Following similar arguments, we can obtain the following form of the secular determinant

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\ H'_{21} & H'_{22}-E_n^{(1)} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & H'_{33}-E_n^{(1)} & H'_{34} & 0 & 0 & 0 & 0 \\ 0 & 0 & H'_{43} & H'_{44}-E_n^{(1)} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H'_{55}-E_n^{(1)} & H'_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & H'_{65} & H'_{66}-E_n^{(1)} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & H'_{77}-E_n^{(1)} & H'_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & H'_{87} & H'_{88}-E_n^{(1)} \end{vmatrix}$$

The above determinant is block diagonal (4 number of 2x2 blocks that are not coupled to each other). The advantage of having block diagonal determinant like this is that we can now, instead of solving an 8 by 8 problem, solve four number of 2 by 2 problems. The latter is much easier. We should keep in mind that only those states which are connected by off-diagonal elements, are coupled to each other via the applied perturbation (electron-electron interaction).

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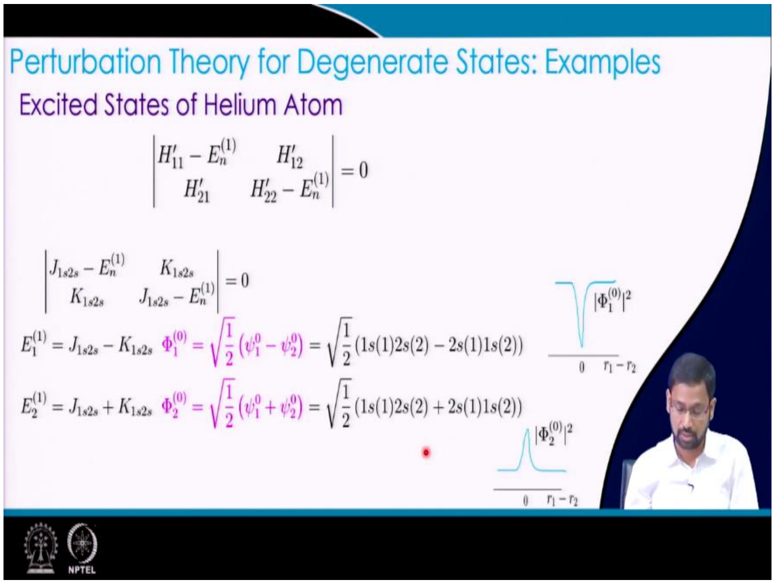


Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} \\ H'_{21} & H'_{22}-E_n^{(1)} \end{vmatrix} = 0$$

$$\begin{vmatrix} J_{1s2s}-E_n^{(1)} & K_{1s2s} \\ K_{1s2s} & J_{1s2s}-E_n^{(1)} \end{vmatrix} = 0$$

$$E_1^{(1)} = J_{1s2s} - K_{1s2s} \quad \Phi_1^{(0)} = \sqrt{\frac{1}{2}}\left(\psi_1^0 - \psi_2^0\right) = \sqrt{\frac{1}{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)$$

$$E_2^{(1)} = J_{1s2s} + K_{1s2s} \quad \Phi_2^{(0)} = \sqrt{\frac{1}{2}}\left(\psi_1^0 + \psi_2^0\right) = \sqrt{\frac{1}{2}}\left(1s(1)2s(2) + 2s(1)1s(2)\right)$$

Now, let us consider the first of the 4 blocks, i.e.,

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} \\ H'_{21} & H'_{22}-E_n^{(1)} \end{vmatrix} = 0$$

We have already determined H'_{11}, H'_{12}, H'_{21}, and H'_{22}. By using those values, we get,

$$\begin{vmatrix} J_{1s2s}-E_n^{(1)} & K_{1s2s} \\ K_{1s2s} & J_{1s2s}-E_n^{(1)} \end{vmatrix} = 0$$

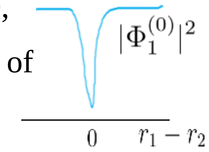
Solving the above 2x2 problem, we get two energy values ($E_1^{(1)}$ and $E_2^{(1)}$) and the corresponding coefficients that are used for describing the zeroth-order wave functions:

$$E_1^{(1)} = J_{1s2s} - K_{1s2s} \quad \Phi_1^{(0)} = \sqrt{\frac{1}{2}}\left(\psi_1^0 - \psi_2^0\right) = \sqrt{\frac{1}{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)$$

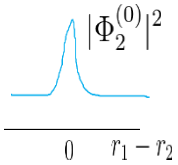
$$E_2^{(1)} = J_{1s2s} + K_{1s2s} \quad \Phi_2^{(0)} = \sqrt{\frac{1}{2}}\left(\psi_1^0 + \psi_2^0\right) = \sqrt{\frac{1}{2}}\left(1s(1)2s(2) + 2s(1)1s(2)\right)$$

Without perturbation, all eight states have same energy. The 1st order energy correction lifts the degeneracy of the two energy levels E_1 and E_2. The 1st order energy corrections involve the Coulomb integral and exchange integral. Corresponding to each of the two energy corrections, we obtain two coefficients. For $E_1^{(1)} = J_{1s2s} – K_{1s2s},$ the two coefficients are $c_1 = -c_2$. Normalization of the wave function results $c_1 = 1/\sqrt{2}$. Similarly, $E_2^{(1)} = J_{1s2s} + K_{1s2s}$, $c_1 = c_2 = 1/\sqrt{2}$.

From the above two wave functions $\left(\Phi_1^{(0)}\ and\ \Phi_2^{(0)}\right)$, it can be seen that when the two electrons approach each other, i.e., r_1-r_2 → 0, 1s(1)2s(2) – 2s(1)1s(2) → 0, hence the wave function approaches 0. In other words, the probability of finding the two electrons at the same spatial position is zero. This goes by the name Fermi hole, i.e., where one electron is located, the other electron would avoid that region.



On the other hand, when r_1-r_2 → 0, $\Phi_2^{(0)}$ does not vanish. Instead, an increase in the probability density is noticed. It shows that if electron number 1 is spatially located somewhere, electron number 2 will have increased probability to be found at the same spatial position. This observation goes by the name Fermi heap.



While Fermi hole is intuitive (i.e., the two electrons avoid each other), Fermi heap is counterintuitive. Although, we may explain Fermi hole as repulsion of like charge, it should be noted that it has nothing to do with the charge of the electron. Both Fermi hole are Fermi heap are quantum mechanical phenomena. We will rationalize these results in our next class.

Thank you for your attention.