Approximate Methods in Quantum Chemistry
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Lecture 22
Degenerate Perturbation Theory

Hello students! Welcome to this lecture. After discussing perturbation theory and its applications to various systems, in this lecture, we will discuss perturbation theory applicable to degenerate states.

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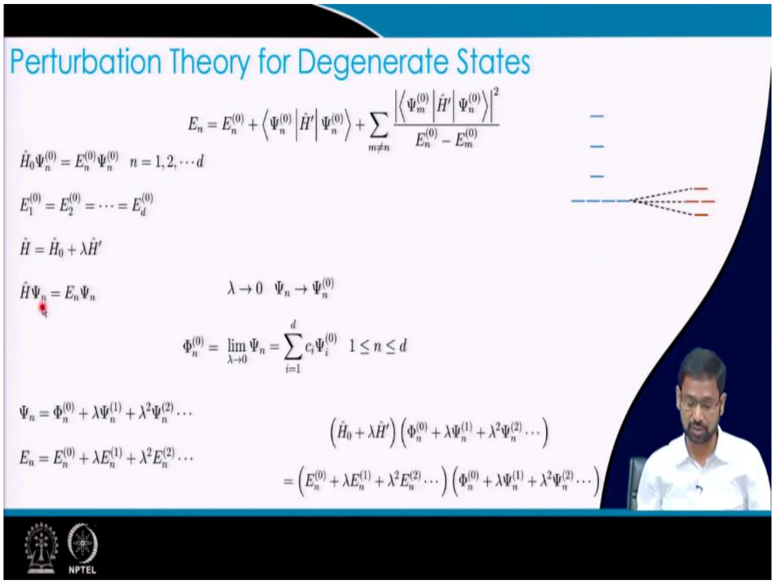

Perturbation Theory for Degenerate States

$$E_n = E_n^{(0)} + \left\langle \Psi_n^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle + \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

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

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

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

$\hat{H} \Psi_n = E_n \Psi_n \qquad \lambda \to 0 \quad \Psi_n \to \Psi_n^{(0)}$

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

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

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

$$\left(\hat{H}_0 + \lambda \hat{H}'\right)\left(\Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \cdots\right)$$
$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \cdots\right)\left(\Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \cdots\right)$$

From perturbation theory, we obtained the energy expression for the n^{th} state as,

$$E_n = E_n^{(0)} + \left\langle \Psi_n^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle + \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

where the first term is the unperturbed energy of the n^{th} state, followed by the 1st and 2nd order energy corrections in the 2nd and 3rd terms, respectively. While the 1st order correction is obtained by evaluating only 1 integral, the 2nd order energy correction requires evaluation of many integrals. In other words, the 2nd order energy correction for the n^{th} state depends on all other states (m), especially on those states who lie close in energy with the state of interest (n), as indicated by the term $E_n^{(0)} - E_m^{(0)}$ in the denominator. What if the states n and m are degenerate? In such a case, we can not use the standard perturbation theory we have discussed so far. Instead, we will devise a way to treat degenerate states with perturbation theory.

Consider a *d*-fold degeneracy, for which we can write down

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

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

If we apply a perturbation to this system, the energy levels and wave functions of the perturbed system are going to change accordingly,

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

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

In such a situation, the degeneracy may be lifted completely, or partially, depending on the nature of the perturbation. When we withdraw this perturbation slowly, we expect the system to come back to its original state. In other words, when $\lambda \to 0 \quad \Psi_n \to \Psi_n^{(0)}$. However, since the states are degenerate in the absence of perturbation, we can express many linear combinations of these degenerate states which will have same energy, i.e.,

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

Hence, for vanishing perturbation we can get some linear combination of the unperturbed degenerate states and express them as $\Phi_n^{(0)}$, representing the unperturbed states. Upon perturbation, we can define the perturbed wave function and energy as:

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

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

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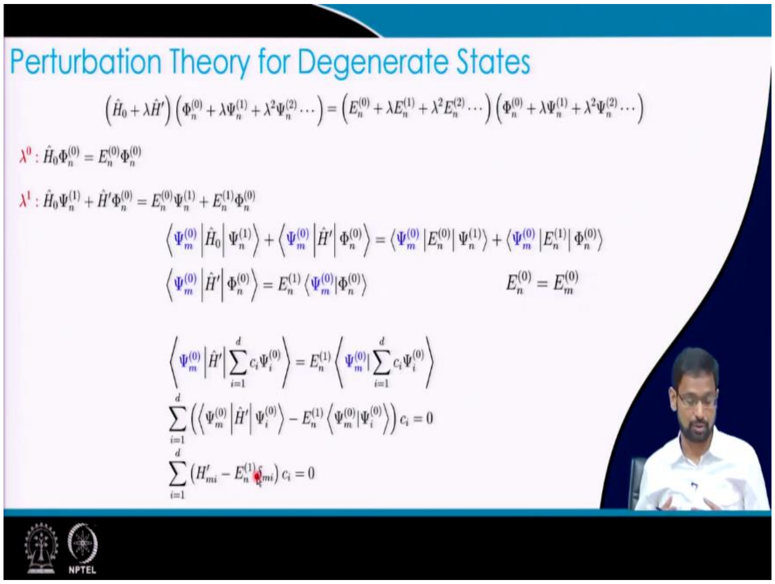

Perturbation Theory for Degenerate States

$$\left(\hat{H}_0+\lambda\hat{H}'\right)\left(\Phi_n^{(0)}+\lambda\Psi_n^{(1)}+\lambda^2\Psi_n^{(2)}\cdots\right)=\left(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}\cdots\right)\left(\Phi_n^{(0)}+\lambda\Psi_n^{(1)}+\lambda^2\Psi_n^{(2)}\cdots\right)$$

$\lambda^0:\hat{H}_0\Phi_n^{(0)}=E_n^{(0)}\Phi_n^{(0)}$

$\lambda^1:\hat{H}_0\Psi_n^{(1)}+\hat{H}'\Phi_n^{(0)}=E_n^{(0)}\Psi_n^{(1)}+E_n^{(1)}\Phi_n^{(0)}$

$$\left\langle\Psi_m^{(0)}\middle|\hat{H}_0\middle|\Psi_n^{(1)}\right\rangle+\left\langle\Psi_m^{(0)}\middle|\hat{H}'\middle|\Phi_n^{(0)}\right\rangle=\left\langle\Psi_m^{(0)}\middle|E_n^{(0)}\middle|\Psi_n^{(1)}\right\rangle+\left\langle\Psi_m^{(0)}\middle|E_n^{(1)}\middle|\Phi_n^{(0)}\right\rangle$$

$$\left\langle\Psi_m^{(0)}\middle|\hat{H}'\middle|\Phi_n^{(0)}\right\rangle=E_n^{(1)}\left\langle\Psi_m^{(0)}\middle|\Phi_n^{(0)}\right\rangle \qquad E_n^{(0)}=E_m^{(0)}$$

$$\left\langle\Psi_m^{(0)}\middle|\hat{H}'\middle|\sum_{i=1}^{d}c_i\Psi_i^{(0)}\right\rangle=E_n^{(1)}\left\langle\Psi_m^{(0)}\middle|\sum_{i=1}^{d}c_i\Psi_i^{(0)}\right\rangle$$

$$\sum_{i=1}^{d}\left(\left\langle\Psi_m^{(0)}\middle|\hat{H}'\middle|\Psi_i^{(0)}\right\rangle-E_n^{(1)}\left\langle\Psi_m^{(0)}\middle|\Psi_i^{(0)}\right\rangle\right)c_i=0$$

$$\sum_{i=1}^{d}\left(H'_{mi}-E_n^{(1)}\delta_{mi}\right)c_i=0$$

Using the above expression in the Schrodinger equation,

$$\left(\hat{H}_0+\lambda\hat{H}'\right)\left(\Phi_n^{(0)}+\lambda\Psi_n^{(1)}+\lambda^2\Psi_n^{(2)}\cdots\right)=\left(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}\cdots\right)\left(\Phi_n^{(0)}+\lambda\Psi_n^{(1)}+\lambda^2\Psi_n^{(2)}\cdots\right)$$

Let us now collect all terms in the above equation that have $\lambda^0$and λ^1 dependence,

$\lambda^0:\hat{H}_0\Phi_n^{(0)}=E_n^{(0)}\Phi_n^{(0)}$

$\lambda^1:\hat{H}_0\Psi_n^{(1)}+\hat{H}'\Phi_n^{(0)}=E_n^{(0)}\Psi_n^{(1)}+E_n^{(1)}\Phi_n^{(0)}$

The first line represents the solution of the unperturbed system. Let us multiply $\left\langle\Psi_m^{(0)}\right|$ from left in the second line above to obtain (*m* is one of the degenerate states),

$$\left\langle\Psi_m^{(0)}\middle|\hat{H}_0\middle|\Psi_n^{(1)}\right\rangle+\left\langle\Psi_m^{(0)}\middle|\hat{H}'\middle|\Phi_n^{(0)}\right\rangle=\left\langle\Psi_m^{(0)}\middle|E_n^{(0)}\middle|\Psi_n^{(1)}\right\rangle+\left\langle\Psi_m^{(0)}\middle|E_n^{(1)}\middle|\Phi_n^{(0)}\right\rangle$$

$$\left\langle\Psi_m^{(0)}\middle|\hat{H}'\middle|\Phi_n^{(0)}\right\rangle=E_n^{(1)}\left\langle\Psi_m^{(0)}\middle|\Phi_n^{(0)}\right\rangle \qquad E_n^{(0)}=E_m^{(0)}$$

The 1st term in the left and right-hand side of the first relation above can be shown to be equal by using the Hermitian nature of $\widehat{H}_0$ and degeneracy of state *n* and *m*. This results in the second relation above, which can be further expressed by using $\Phi_n^{(0)}=\sum_{i=1}^{d}c_i\,\Psi_i^{(0)}$,

$$\left\langle \Psi_m^{(0)} \left| \hat{H}' \right| \sum_{i=1}^{d} c_i \Psi_i^{(0)} \right\rangle = E_n^{(1)} \left\langle \Psi_m^{(0)} \right| \sum_{i=1}^{d} c_i \Psi_i^{(0)} \right\rangle$$

$$\sum_{i=1}^{d} \left(\left\langle \Psi_m^{(0)} \left| \hat{H}' \right| \Psi_i^{(0)} \right\rangle - E_n^{(1)} \left\langle \Psi_m^{(0)} | \Psi_i^{(0)} \right\rangle \right) c_i = 0$$

$$\sum_{i=1}^{d} \left(H'_{mi} - E_n^{(1)} \delta_{mi} \right) c_i = 0$$

Now, we have *d* number of linearly dependent equations, whose solutions would give us the 1st order energy corrections.

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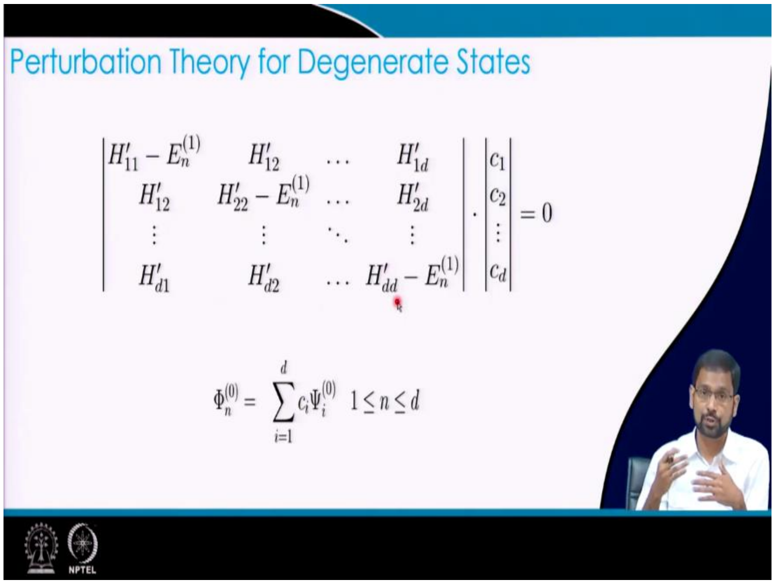

Perturbation Theory for Degenerate States

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

$$\Phi_n^{(0)} = \sum_{i=1}^{d} c_i \Psi_i^{(0)} \quad 1 \leq n \leq d$$

We can express the secular equation as the *d* x *d* determinant shown in the slide above. The solution of these secular equations would result in *d* number of energy values representing the first order energy corrections for each of the *d*-degenerate states. For each energy value, we would get a set of coefficients c_1, c_2, … c_d which would be used in expressing the zeroth-order wave function for that energy level.

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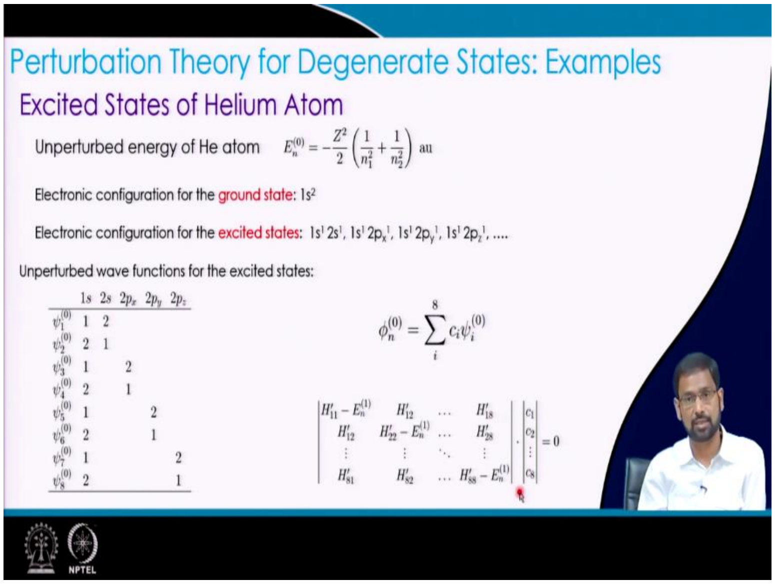

Perturbation Theory for Degenerate States: Examples

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

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

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

Now, let us apply the degenerate perturbation theory to the excited states of helium atom. If we consider the electron-electron repulsion in He atom as perturbation, the unperturbed energy would be (equal to two hydrogenic atoms with $Z = 2$)

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

where, n_1 and n_2 are the principal quantum numbers of the two electrons. The ground state is obtained when $n_1 = n_2 = 1$ (electronic configuration: $1s^2$). The excited states are obtained by promoting one electron to $n_2 = 2$. We can generate four such configurations: $1s^12s^1$, $1s^12p_x^1$, $1s^12p_y^1$, and $1s^12p_z^1$. To allow electron indistinguishability, we can generate another four electron configurations where electron 1 and 2 are exchanged. In total, we obtain following 8 electronic configurations that would have same energy (in the absence of electron-electron interaction):

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
$\psi_1^{(0)}$	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

These 8-fold degenerate system can be represented by wave functions ($\phi_n^{(0)}$) as

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

This would result in 8-linearly dependent equations, which can be represented by

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

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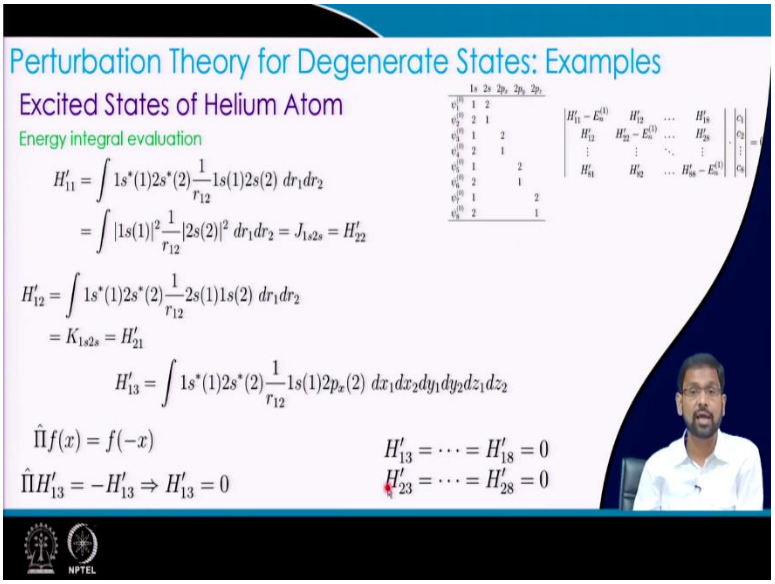

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Energy integral evaluation

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

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

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

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

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

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

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

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
$\psi_1^{(0)}$	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

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

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

$$\begin{aligned} H'_{12} &= \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}2s(1)1s(2)\ dr_1 dr_2 \\ &= K_{1s2s} = H'_{21} \end{aligned}$$

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

$$H'_{13} = \int 1s^*(1)2s^*(2)\frac{1}{r_{12}}1s(1)2p_x(2)\ dx_1 dx_2 dy_1 dy_2 dz_1 dz_2$$

In the above integral, instead of writing $\mathrm{d}r_1$ $\mathrm{d}r_2$, we have actually expanded it in terms of $\mathrm{d}x_1$ $\mathrm{d}y_1$ $\mathrm{d}z_1$ for electron 1 and similarly $\mathrm{d}x_2$ $\mathrm{d}y_2$ $\mathrm{d}z_2$ 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 hence vanishes. Similarly, we can show that not only H'_{13}, but also $H'_{14} = H'_{15} = H'_{16} = H'_{17} = H'_{18} = 0$. Similarly, $H'_{23} = \ldots = H'_{28} = 0$.

We still have a few more integrals to evaluate before we can solve the secular determinant. We will take that up in our next lecture.

Thank you for your attention.