Approximate Methods in Quantum Chemistry

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Lecture 12

Variational Method in Chemical Bonding - I

Hello students! Welcome to this lecture. In last few lectures, we have been discussing variational principle and in particular the linear variational method and its applications. In this lecture, we would apply linear variational principle in one of the most important topics in chemistry: chemical bonding.

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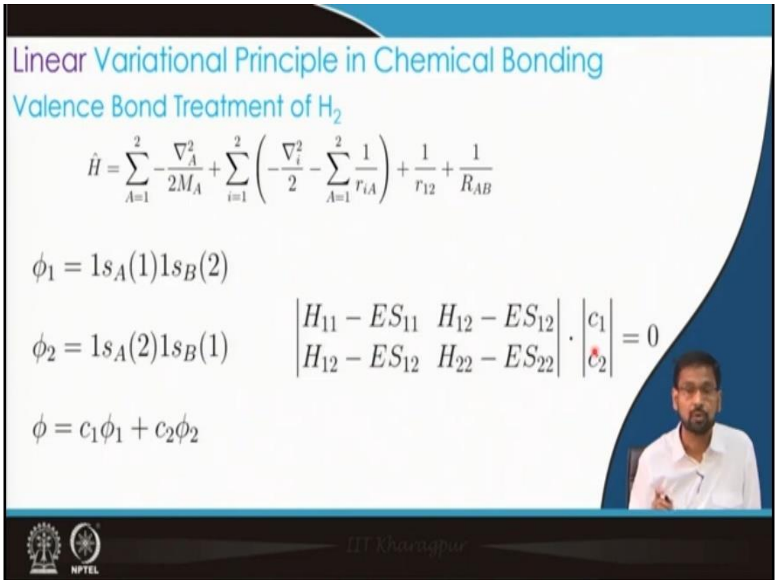

Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$$\hat{H} = \sum_{A=1}^{2} -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \sum_{A=1}^{2}\frac{1}{r_{iA}}\right) + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

Our first example system is the hydrogen molecule. In the previous lecture we discussed the Hamiltonian of the molecule and formed the trial function as a linear combination of two functions, each of which were obtained from the 1s functions of the constituent atoms. This trial function ensured the indistinguishability of the electrons in a molecule.

With the given Hamiltonian and the trial function, we can try to solve the problem using linear variational method. To that end, we would first obtain the overlap and Hamiltonian matrix elements.

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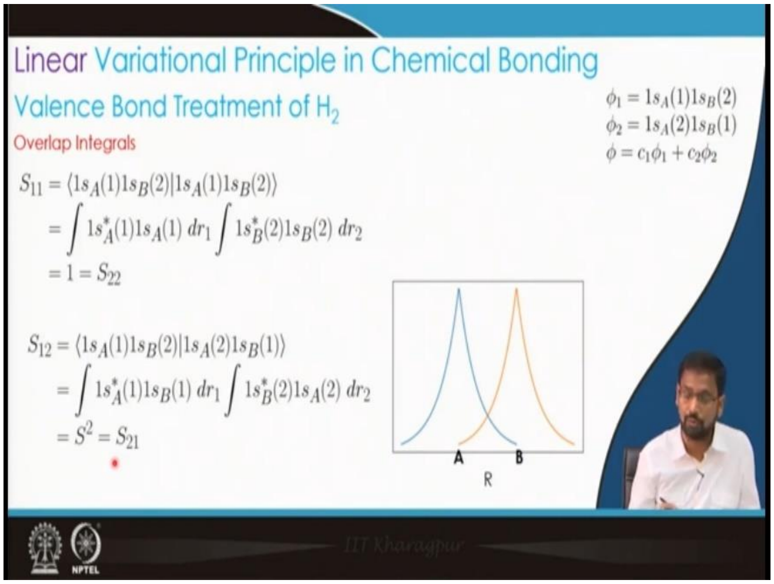

Linear Variational Principle in Chemical Bonding

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Overlap Integrals

$$\phi_1 = 1s_A(1)1s_B(2)$$
$$\phi_2 = 1s_A(2)1s_B(1)$$
$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\begin{aligned} S_{11} &= \langle 1s_A(1)1s_B(2)|1s_A(1)1s_B(2)\rangle \\ &= \int 1s_A^*(1)1s_A(1)\,dr_1 \int 1s_B^*(2)1s_B(2)\,dr_2 \\ &= 1 = S_{22} \end{aligned}$$

$$\begin{aligned} S_{12} &= \langle 1s_A(1)1s_B(2)|1s_A(2)1s_B(1)\rangle \\ &= \int 1s_A^*(1)1s_B(1)\,dr_1 \int 1s_B^*(2)1s_A(2)\,dr_2 \\ &= S^2 = S_{21} \end{aligned}$$

First, we will discuss the overlap integrals. The term S_{11} can be written as the overlap of ϕ_1 with itself, as shown below:

$$\begin{aligned} S_{11} &= \langle 1s_A(1)1s_B(2)|1s_A(1)1s_B(2)\rangle \\ &= \int 1s_A^*(1)1s_A(1)\,dr_1 \int 1s_B^*(2)1s_B(2)\,dr_2 \\ &= 1 = S_{22} \end{aligned}$$

Here the terms depending on electron 1 and electron 2 are integrated separately as they are independent variables. Each of the integral is 1, since the $1s_A$ and $1s_B$ functions are normalized.

Next, we determine the overlap integral S_{12} following a similar approach:

$$\begin{aligned} S_{12} &= \langle 1s_A(1)1s_B(2)|1s_A(2)1s_B(1)\rangle \\ &= \int 1s_A^*(1)1s_B(1)\,dr_1 \int 1s_B^*(2)1s_A(2)\,dr_2 \\ &= S^2 = S_{21} \end{aligned}$$

Here each integral (for electron 1 or 2), contains $1s_A$ and $1s_B$ functions, which are eigenfunctions of two different systems (atom A and B). Hence, they are not orthogonal. Rather their overlap integral has some finite value depending on the relative separation of the two nuclei. When the two nuclei come closer to each other, this overlap integral will become larger and in the hypothetical situation where both atoms are on top of each other, the overlap becomes 1. With increasing separation of the nuclei, the overlap integral decreases and eventually becomes 0 when the atoms are well separated (see the figure in the slide above). Hence, for a given inter-nuclear separation (R), each integral in the overlap integral expression above becomes a constant (S) and the value of $S_{12} = S^2 = S_{21}$.

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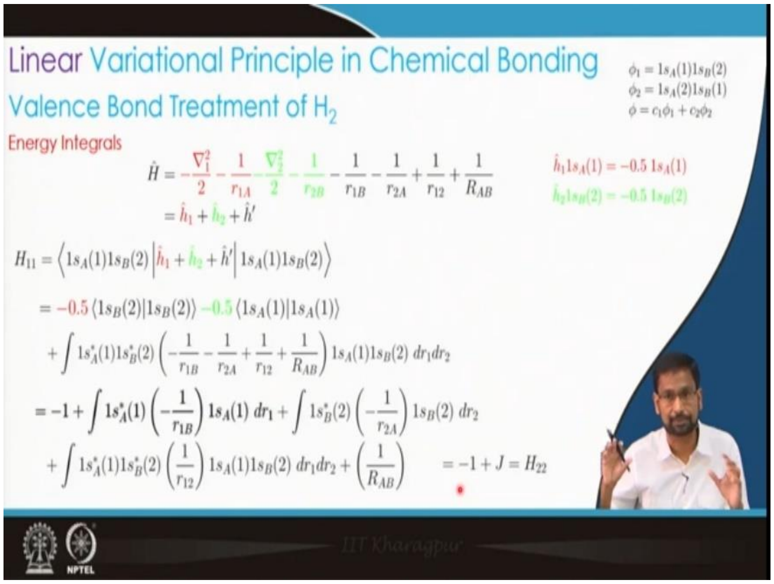

Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$\phi_1 = 1s_A(1)1s_B(2)$
$\phi_2 = 1s_A(2)1s_B(1)$
$\phi = c_1\phi_1 + c_2\phi_2$

Energy Integrals

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} = \hat{h}_1 + \hat{h}_2 + \hat{h}'$$

$\hat{h}_1 1s_A(1) = -0.5\ 1s_A(1)$
$\hat{h}_2 1s_B(2) = -0.5\ 1s_B(2)$

$$\begin{aligned} H_{11} &= \left\langle 1s_A(1)1s_B(2) \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}' \middle| 1s_A(1)1s_B(2) \right\rangle \\ &= -0.5 \langle 1s_B(2)|1s_B(2)\rangle - 0.5 \langle 1s_A(1)|1s_A(1)\rangle \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(1)1s_B(2)\, dr_1 dr_2 \\ &= -1 + \int 1s_A^*(1) \left(-\frac{1}{r_{1B}} \right) 1s_A(1)\, dr_1 + \int 1s_B^*(2) \left(-\frac{1}{r_{2A}} \right) 1s_B(2)\, dr_2 \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}} \right) 1s_A(1)1s_B(2)\, dr_1 dr_2 + \left(\frac{1}{R_{AB}} \right) \quad = -1 + J = H_{22} \end{aligned}$$

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Now, let us look at the energy integrals. First let us evaluate $H_{11} = \langle \phi_1 | \hat{H} | \phi_1 \rangle$. Here the Hamiltonian (within Born-Oppenheimer approximation) has the following form:

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= \hat{h}_1 + \hat{h}_2 + \hat{h}'$$

where the first two terms (h_1 in red) constitute the Hamiltonian of atom A and the next two terms (h_2 in green) describe the Hamiltonian of atom B, whose solutions are given below

$$\hat{h}_1 1s_A(1) = -0.5\ 1s_A(1)$$
$$\hat{h}_2 1s_B(2) = -0.5\ 1s_B(2)$$

The remaining four terms appear due to the interaction of the two atoms (both for nuclei and electrons). These terms are absent when there is no chemical bond.

Now we can evaluate H_{11}

$$H_{11} = \left\langle 1s_A(1)1s_B(2) \left| \hat{h}_1 + \hat{h}_2 + \hat{h}' \right| 1s_A(1)1s_B(2) \right\rangle$$

First consider the action of h_1 and h_2 operators (using the fact that $1s_A$ $1s_B$ are their eigenfunctions),

$$= -0.5 \left\langle 1s_B(2)|1s_B(2)\right\rangle -0.5 \left\langle 1s_A(1)|1s_A(1)\right\rangle$$

Each of the above terms gives -0.5 (au).

This leaves us with the action of h', which is given below

$$\int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}\right) 1s_A(1)1s_B(2)\ dr_1 dr_2$$

The above expression requires evaluation of 4 integrals (one for each operator). When we evaluate these integrals, we should separate the terms that depend on electron 1 and electron 2 and integrate them separately. For example, for $-1/r_{1B}$ term we can write

$$\int 1s_A^*(1) \left(-\frac{1}{r_{1B}}\right) 1s_A(1)\ dr_1$$

where we have used $\int 1s_B^*(2)1s_B(2)dr_2 = 1$ to obtain the above expression. We can do similar exercise for other terms to obtain H_{11} as

$$\begin{aligned} &= -1 + \int 1s_A^*(1) \left(-\frac{1}{r_{1B}}\right) 1s_A(1)\ dr_1 + \int 1s_B^*(2) \left(-\frac{1}{r_{2A}}\right) 1s_B(2)\ dr_2 \\ &+ \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}}\right) 1s_A(1)1s_B(2)\ dr_1 dr_2 + \left(\frac{1}{R_{AB}}\right) \end{aligned}$$

The first term -1 appears from h1 and h2 part of the Hamiltonian, which represents the energy expectation value when the two atoms are well separated. The second term represents the attractive Coulomb interaction between the nucleus B and the electron density corresponding to electron 1 (present in nucleus A). Similarly, the third term represents the attractive Coulomb interaction between the nucleus A and the electron density corresponding to electron 2 (present in nucleus B). The last two terms are repulsive Coulomb interaction between the two electrons and the two nuclei. The last four terms of the above expression are together called the Coulomb integral (J), which has a definite value for a fixed inter-nuclear distance. Hence, $H_{11} = -1 + J(R) = H_{22}$.

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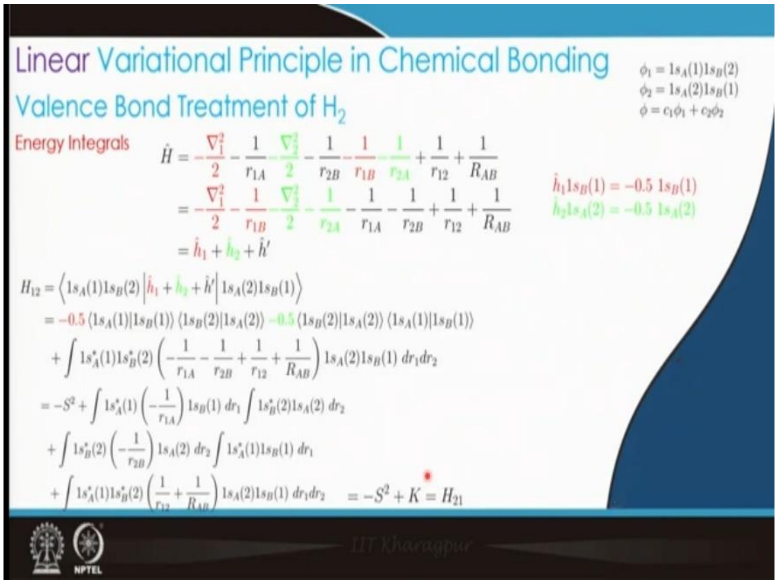

Linear Variational Principle in Chemical Bonding

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$\phi_2 = 1s_A(2)1s_B(1)$
$\phi = c_1\phi_1 + c_2\phi_2$

Energy Integrals

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1B}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2A}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= \hat{h}_1 + \hat{h}_2 + \hat{h}'$$

$\hat{h}_1 1s_B(1) = -0.5\ 1s_B(1)$
$\hat{h}_2 1s_A(2) = -0.5\ 1s_A(2)$

$$H_{12} = \left\langle 1s_A(1)1s_B(2) \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}' \middle| 1s_A(2)1s_B(1) \right\rangle$$
$$= -0.5 \langle 1s_A(1)|1s_B(1)\rangle \langle 1s_B(2)|1s_A(2)\rangle - 0.5 \langle 1s_B(2)|1s_A(2)\rangle \langle 1s_A(1)|1s_B(1)\rangle$$
$$+ \int 1s_A^*(1)1s_B^*(2)\left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}\right) 1s_A(2)1s_B(1)\, dr_1 dr_2$$
$$= -S^2 + \int 1s_A^*(1)\left(-\frac{1}{r_{1A}}\right) 1s_B(1)\, dr_1 \int 1s_B^*(2)1s_A(2)\, dr_2$$
$$+ \int 1s_B^*(2)\left(-\frac{1}{r_{2B}}\right) 1s_A(2)\, dr_2 \int 1s_A^*(1)1s_B(1)\, dr_1$$
$$+ \int 1s_A^*(1)1s_B^*(2)\left(\frac{1}{r_{12}} + \frac{1}{R_{AB}}\right) 1s_A(2)1s_B(1)\, dr_1 dr_2 \quad = -S^2 + K = H_{21}$$

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Next, we evaluate H_{12}. Just like the previous case, we will simplify the total Hamiltonian to a few simple terms:

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1B}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2A}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= \hat{h}_1 + \hat{h}_2 + \hat{h}'$$

The h_1 and h_2 are rearranged in a slightly different way compared to the previous case (H_{11}). This has been done by keeping the form of the function in the ket (here it is $\phi_2 = 1s_{A(2)}1s_{B(1)}$), such that we can write the following (by realizing that $1s_B(1)$ is now eigenfunction of h_1 and $1s_A(2)$ is the eigenfunction of h_2):

$$\hat{h}_1 1s_B(1) = -0.5\ 1s_B(1)$$
$$\hat{h}_2 1s_A(2) = -0.5\ 1s_A(2)$$

After taking care of h_1 and h_2, we are left with four terms (h'). Following the same procedure as earlier (evaluating the integrals by separating the terms dependent on r_1 and r_2), we obtain

$$
\begin{aligned}
H_{12} &= \left\langle 1s_A(1)1s_B(2) \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}' \middle| 1s_A(2)1s_B(1) \right\rangle \\
&= -0.5 \left\langle 1s_A(1)|1s_B(1)\right\rangle \left\langle 1s_B(2)|1s_A(2)\right\rangle -0.5 \left\langle 1s_B(2)|1s_A(2)\right\rangle \left\langle 1s_A(1)|1s_B(1)\right\rangle \\
&\quad + \int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}\right) 1s_A(2)1s_B(1)\; dr_1 dr_2
\end{aligned}
$$

h_1 acts on its eigenfunction ($1s_B(1)$) leaving behind two overlap integrals (each of which has been earlier defined as S) resulting in $-0.5S^2$. Similarly, the second term (related to h_2) yields $-0.5\ S^2$. Next, we consider the third term which is sum of four different integrals. Each of these integrals is a product of two integrals (one for variable r_1 and the other for r_2). Take for example, $-(1/r_{1A})$ operator (which depends on electron 1), we can collect all terms with electron 1 dependence and all terms with electron 2 dependence and then integrate them separately, as shown below:

$$
\int 1s_A^*(1) \left(-\frac{1}{r_{1A}}\right) 1s_B(1)\; dr_1 \int 1s_B^*(2)1s_A(2)\; dr_2
$$

When we look at the first integral above we see that electron 1 is exchanged between A and B atoms (in left- and right-hand side of the operator). Unlike the previous case of $H_{11,}$ where we defined a Coulomb integral, here we can not have a physical description of the electron. This is a pure quantum phenomenon that appears in our equations, because we have ϕ_2 in our trial function which exchanges the two electrons. Similarly, we can show it for the rest of the terms in our Hamiltonian:

$$
\begin{aligned}
&+ \int 1s_B^*(2) \left(-\frac{1}{r_{2B}}\right) 1s_A(2)\; dr_2 \int 1s_A^*(1)1s_B(1)\; dr_1 \\
&+ \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}} + \frac{1}{R_{AB}}\right) 1s_A(2)1s_B(1)\; dr_1 dr_2
\end{aligned}
$$

Together, these integrals are called ‘exchange integral’ (K). All of them they appear due to the exchange of electrons upon chemical bonding. Just like the Coulomb integral (J), the exchange integral also appears when the two atoms come closer and make a bond. But when they are well separated both these integrals vanish. In other words, like Coulomb integral, the exchange integral also is a function of inter-nuclear separation (R).

In our next class, we will use these integrals and continue our discussion on valence bond theory.

Thank you for your attention.